Aspen Physical Property System

Physical Property Methods

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Aspen Technology, Inc.
20 Crosby Drive
Bedford, MA 01730
USA
Phone: (1) (781) 221-6400
Toll Free: (1) (888) 996-7100
URL: http://www.aspentech.com

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1 Overview of Aspen Physical Property Methods

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All unit operation models need property calculations to generate results. The most often requested properties are fugacities for thermodynamic equilibrium (flash calculation). Enthalpy calculations are also often requested. Fugacities and enthalpies are often sufficient information to calculate a mass and heat balance. However, other thermodynamic properties (and, if requested, transport properties) are calculated for all process streams.

The impact of property calculation on the calculation result is great. This is due to the quality and the choice of the equilibrium and property calculations. Equilibrium calculation and the bases of property calculation are explained in this chapter. The understanding of these bases is important to choose the appropriate property calculation. Property Method Descriptions gives more help on this subject. The quality of the property calculation is determined by the model equations themselves and by the usage. For optimal usage, you may need details on property calculation. These are given in Physical Calculation Methods and Routes and *Physical Property Models*.

Later sections cover more specific topics: Electrolyte Calculation, Free-Water and Rigorous Three-Phase Calculations, Petroleum Components Characterization Methods, and Property Parameter Estimation.

This chapter contains three sections:

- Thermodynamic property methods
- Transport property methods
- Nonconventional component enthalpy calculation

The thermodynamic property methods section discusses the two methods of calculating vapor-liquid equilibrium (VLE): the equation-of-state method and the activity coefficient method. Each method contains the following:

- Fundamental concepts of phase equilibria and the equations used
- Application to vapor-liquid equilibria and other types of equilibria, such as liquid-liquid
- Calculations of other thermodynamic properties

The last part of this section gives an overview of the current equation of state and activity coefficient technology.

See the table labeled Symbol Definitions in the section Nonconventional Component Enthalpy Calculation for definitions of the symbols used in equations.

Thermodynamic Property Methods

The key thermodynamic property calculation performed in a calculation is phase equilibrium. The basic relationship for every component *i* in the vapor and liquid phases of a system at equilibrium is:

$$f_i^v = f_i^l \qquad (1)$$

Where:

f_i^v = Fugacity of component *i* in the vapor phase

f_i^l = Fugacity of component *i* in the liquid phase

Applied thermodynamics provides two methods for representing the fugacities from the phase equilibrium relationship in terms of measurable state variables, the equation-of-state method and the activity coefficient method.

In the equation of state method:

$$f_i^v = \varphi_i^v y_i p \qquad (2)$$

$$f_i^l = \varphi_i^l x_i p \qquad (3)$$

With:

$$\ln \varphi_i^\alpha = -\frac{1}{RT} \int_\infty^{V\alpha} \left[\left(\frac{\partial p}{\partial n_i} \right)_{T,V,n_{iej}} - \frac{RT}{V} \right] dV - \ln Z_m^\alpha \qquad (4)$$

Where:

α = v or l

V = Total volume

n_i = Mole number of component *i*

Equations 2 and 3 are identical with the only difference being the phase to which the variables apply. The fugacity coefficient φ_i^α is obtained from the equation of state, represented by *p* in equation 4. See equation 45 for an example of an equation of state.

In the activity coefficient method:

$$f_i^v = \varphi_i^v y_i p \qquad (5)$$

$$f_i^l = x_i \gamma_i f_i^{*,l} \tag{6}$$

Where φ_i^v is calculated according to equation 4,

γ_i = Liquid activity coefficient of component *i*

$f_i^{*,l}$ = Liquid fugacity of pure component *i* at mixture temperature

Equation 5 is identical to equation 2. Again, the fugacity coefficient is calculated from an equation of state. Equation 6 is totally different.

Each property method in the Aspen Physical Property System is based on either the equation-of-state method or the activity coefficient method for phase equilibrium calculations. The phase equilibrium method determines how other thermodynamic properties, such as enthalpies and molar volumes, are calculated.

With an equation-of-state method, all properties can be derived from the equation of state, for both phases. Using an activity coefficient method, the vapor phase properties are derived from an equation of state, exactly as in the equation-of- state method. However the liquid properties are determined from summation of the pure component properties to which a mixing term or an excess term is added.

Enthalpy Calculation

The enthalpy reference state used by the Aspen Physical Property System for a compound is that of the constituent elements in their standard states at 298.15 K and 1 atm. Because of this choice of reference state, the actual values of enthalpy calculated by the Aspen Physical Property System may be different from those calculated by other programs. All enthalpy differences, however, should be similar to those calculated by other programs.

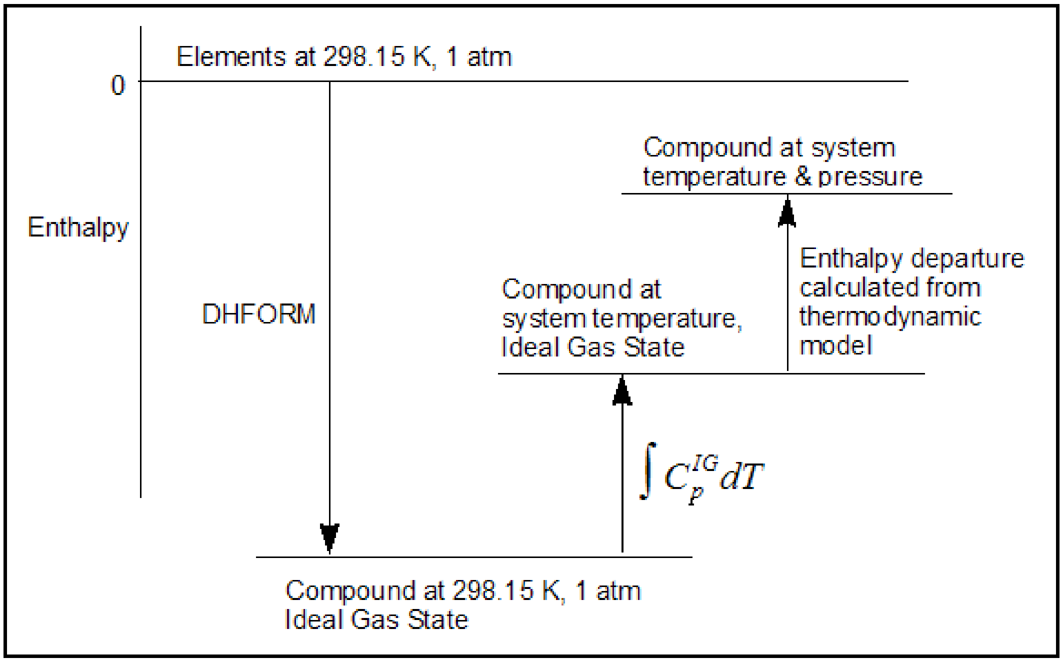
The enthalpy of a compound at a given temperature and pressure is calculated as the sum of the following three quantities:

- Enthalpy change involved in reacting the elements at 298.15 K and 1 atm at their reference state (vapor, liquid or solid) conditions to form the compound at 298.15 K and ideal gas conditions. This quantity is called enthalpy of formation (DHFORM) in the Aspen Physical Property System.
- Enthalpy change involved in taking the compound from 298.15 K and 1 atm to system temperature still at ideal gas conditions. This quantity is calculated as:

  $$\int_{298.15}^{T} C_p^{IG} dT$$

- Enthalpy change involved in taking the compound to system pressure and state. This is called the enthalpy departure, either DHV (vapor state), DHL (liquid state), or DHS (solid state), and is symbolically shown as the difference in the enthalpies, such as ($H_i^{*,l}$ - $H_i^{*,ig}$) for liquid enthalpy departure. The method of calculation of this value varies depending on the thermodynamic model used to represent the vapor and liquid phases.

These three steps are shown graphically in the diagram below:



Equation-of-State Method

The partial pressure of a component *i* in a gas mixture is:

$$p_i = y_i p \tag{7}$$

The fugacity of a component in an ideal gas mixture is equal to its partial pressure. The fugacity in a real mixture is the effective partial pressure:

$$f_i^v = \varphi_i^v y_i p \tag{8}$$

The correction factor φ_i^v is the fugacity coefficient. For a vapor at moderate pressures, φ_i^v is close to unity. The same equation can be applied to a liquid:

$$f_i^l = \varphi_i^l y_i p \tag{9}$$

A liquid differs from an ideal gas much more than a real gas differs from an ideal gas. Thus fugacity coefficients for a liquid are very different from unity. For example, the fugacity coefficient of liquid water at atmospheric pressure and room temperature is about 0.03 (Haar et al., 1984).

An equation of state describes the pressure, volume and temperature (p,V,T) behavior of pure components and mixtures. Usually it is explicit in pressure. Most equations of state have different terms to represent attractive and repulsive forces between molecules. Any thermodynamic property, such as fugacity coefficients and enthalpies, can be calculated from the equation of state.

Equation-of-state properties are calculated relative to the ideal gas properties of the same mixture at the same conditions. See Calculation of Properties Using an Equation-of-State Property Method.

Vapor-Liquid Equilibria (Equation-of-State Methods)

The relationship for vapor-liquid equilibrium is obtained by substituting equations 8 and 9 in equation 1 and dividing by *p*:

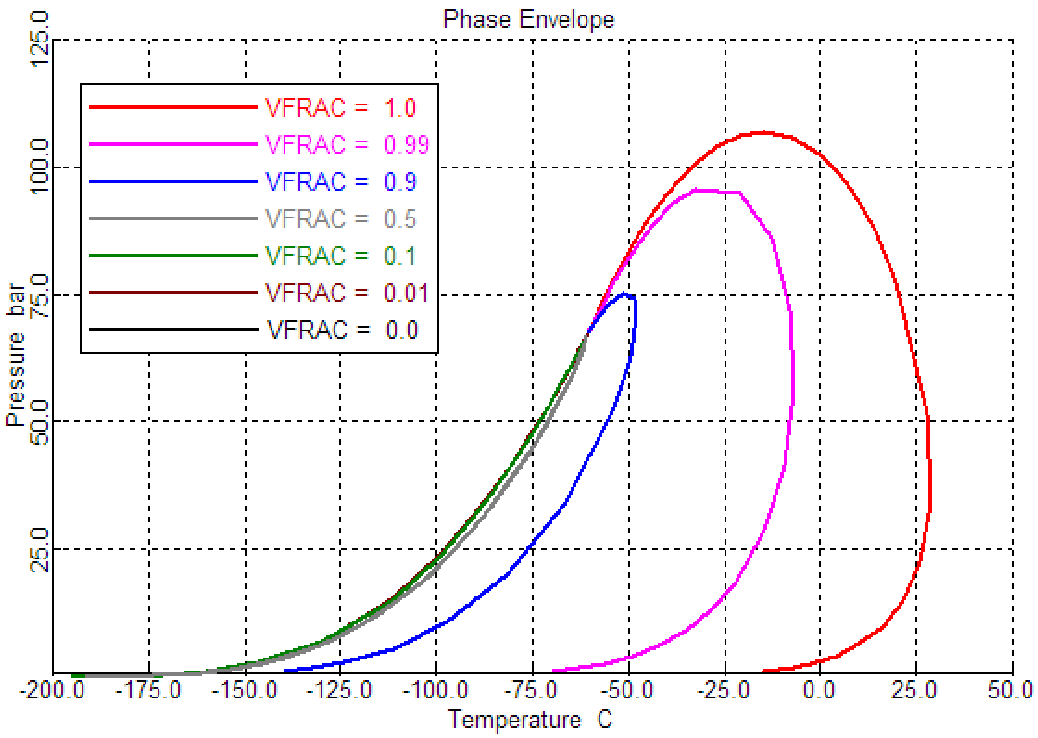
$$\varphi_i^v y_i = \varphi_i^l x_i \tag{10}$$

Fugacity coefficients are obtained from the equation of state (see equation 4 and Calculation of Properties Using an Equation-of-State Property Method). The calculation is the same for supercritical and subcritical components (see Activity Coefficient Method).

Pressure-Temperature Diagram

Fluid phase equilibria depend not only on temperature but also on pressure. At constant temperature (and below the mixture critical temperature), a multi-component mixture will be in the vapor state at very low pressure and in the liquid state at very high pressure. There is an intermediate pressure range for which vapor and liquid phases co-exist. Coming from low pressures, first a dew point is found. Then more and more liquid will form until the vapor disappears at the bubble point pressure. This is illustrated in the figure labeled Phase Envelope of a Methane-Rich Hydrocarbon Mixture. Curves of constant vapor fraction (0.0, 0.01, 0.1, 0.5, 0.9, 0.99, and 1.0) are plotted as a function of temperature. A vapor fraction of unity corresponds to a dew-point; a vapor fraction of zero corresponds to a bubble point. The area confined between dew-point and bubble-point curves is the two-phase region. The dew-point and bubble-point curves meet at high temperatures and pressures at the critical point. The other lines of constant vapor fractions meet at the same point. In Phase Envelope of a Methane-Rich Hydrocarbon Mixture, the critical point is found at a pressure below the maximum of the phase envelope (cricondenbar).

At the critical point the differences between vapor and liquid vanish; the mole fractions and properties of the two phases become identical. Equation 10 can handle this phenomenon because the same equation of state is used to evaluate φ_i^v and φ_i^l. Engineering type equations of state can model the pressure dependence of vapor-liquid equilibria very well. However, they cannot yet model critical phenomena accurately (see Equation-of-State Models).



Phase Envelope of a Methane-Rich Hydrocarbon Mixture

Retrograde Condensation

Compressing the methane-rich mixture shown in the figure labeled Phase Envelope of a Methane-Rich Hydrocarbon Mixture at 270 K (above the mixture critical temperature) will show a dew-point. Then liquid will be formed up to a vapor fraction of about 0.99 (60 bar). Upon further compression the vapor fraction will decrease again until a second dew-point is reached. If the process is carried out with decreasing pressure, liquid is formed when expanding. This is the opposite of the more usual condensation upon compression. It is called retrograde condensation and it happens often in natural gas mixtures.

Liquid-Liquid and Liquid-Liquid-Vapor Equilibria (Equation-of-State Method)

Liquid-liquid equilibria are less pressure dependent than vapor-liquid equilibria, but certainly not pressure independent. The activity coefficient method can model liquid-liquid and liquid-liquid-vapor equilibria at low pressure as a function of temperature. However, with varying pressure the equation of state method is needed (compare Activity Coefficient Method, Liquid-Liquid and Liquid-Liquid-Vapor Equilibria). The equation-of-state method (equation 10) can be applied to liquid-liquid equilibria:

$$\varphi_i^{l1} x_i^{l1} = \varphi_i^{l2} x_i^{l2} \qquad (11)$$

and also to liquid-liquid-vapor equilibria:

$$\varphi_i^{v} y_i = \varphi_i^{l1} x_i^{l1} = \varphi_i^{l2} x_i^{l2} \quad (12)$$

Fugacity coefficients in all the phases are calculated using the same equation of state. Fugacity coefficients from equations of state are a function of composition, temperature, and pressure. Therefore, the pressure dependency of liquid-liquid equilibria can be described.

Liquid Phase Nonideality

Liquid-liquid separation occurs in systems with very dissimilar molecules. Either the size or the intermolecular interactions between components may be dissimilar. Systems that demix at low pressures, have usually strongly dissimilar intermolecular interactions, as for example in mixtures of polar and non-polar molecules. In this case, the miscibility gap is likely to exist at high pressures as well. An examples is the system dimethyl-ether and water (Pozo and Street, 1984). This behavior also occurs in systems of a fully- or near fully-fluorinated aliphatic or alicyclic fluorocarbon with the corresponding hydrocarbon (Rowlinson and Swinton, 1982), for example cyclohexane and perfluorocyclohexane (Dyke et al., 1959; Hicks and Young, 1971).

Systems which have similar interactions, but which are very different in size, do demix at higher pressures. For binary systems, this happens often in the vicinity of the critical point of the light component (Rowlinson and Swinton, 1982).

Examples are:

- Methane with hexane or heptane (van der Kooi, 1981; Davenport and Rowlinson, 1963; Kohn, 1961)
- Ethane with n-alkanes with carbon numbers from 18 to 26 (Peters et al., 1986)
- Carbon dioxide with n-alkanes with carbon numbers from 7 to 20 (Fall et al., 1985)

The more the demixing compounds differ in molecular size, the more likely it is that the liquid-liquid and liquid-liquid-vapor equilibria will interfere with solidification of the heavy component. For example, ethane and pentacosane or hexacosane show this. Increasing the difference in carbon number further causes the liquid-liquid separation to disappear. For example in mixtures of ethane with n-alkanes with carbon numbers higher than 26, the liquid-liquid separation becomes metastable with respect to the solid-fluid (gas or liquid) equilibria (Peters et al., 1986). The solid cannot be handled by an equation-of-state method.

Critical Solution Temperature

In liquid-liquid equilibria, mutual solubilities depend on temperature and pressure. Solubilities can increase or decrease with increasing or decreasing temperature or pressure. The trend depends on thermodynamic mixture properties but cannot be predicted *a priori*. Immiscible phases can become miscible with increasing or decreasing temperature or pressure. In that case a liquid-liquid critical point occurs. Equations 11 and 12 can handle this behavior, but engineering type equations of state cannot model these phenomena accurately.

Calculation of Properties Using an Equation-of-State Property Method

The equation of state can be related to other properties through fundamental thermodynamic equations :

- Fugacity coefficient:

$$f_i^v = \varphi_i^v y_i p \tag{13}$$

- Enthalpy departure:

$$\left(H_m - H_m^{ig}\right) = -\int_{\infty}^{V}\left(p - \frac{RT}{V}\right)dV - RT\ln\left(\frac{V}{V^{ig}}\right) + T\left(S_m - S_m^{ig}\right) + RT\left(Z_m - 1\right) \tag{14}$$

- Entropy departure:

$$\left(S_m - S_m^{ig}\right) = -\int_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_v - \frac{R}{V}\right]dV + R\ln\left(\frac{V}{V^{ig}}\right) \tag{15}$$

- Gibbs energy departure:

$$\left(G_m - G_m^{ig}\right) = -\int_{\infty}^{V}\left(p - \frac{RT}{V}\right)dV - RT\ln\left(\frac{V}{V^{ig}}\right) + RT\left(Z_m - 1\right) \tag{16}$$

- Molar volume:
  Solve *p*(T,V_m) for V_m.

From a given equation of state, fugacities are calculated according to equation 13. The other thermodynamic properties of a mixture can be computed from the departure functions:

- Vapor enthalpy:

$$H_m^v = H_m^{ig} + \left(H_m^v - H_m^{ig}\right) \tag{17}$$

- Liquid enthalpy:

$$H_m^v = H_m^{ig} + \left(H_m^v - H_m^{ig}\right) \tag{18}$$

The molar ideal gas enthalpy, H_m^{ig} is computed by the expression:

$$H_m^{ig} = \sum_i y_i\left[\Delta_f H_i^{ig} + \int_{T^{ref}}^{T} C_{p,i}^{ig}(T)\,dT\right] \tag{19}$$

Where:

$C_{p,i}^{ig}$ = Ideal gas heat capacity

$\Delta_f H_i^{ig}$ = Standard enthalpy of formation for ideal gas at 298.15 K and 1 atm

T^{ref} = Reference temperature = 298.15 K

Entropy and Gibbs energy can be computed in a similar manner:

$$G_m^v = G_m^{ig} + \left(G_m^v - G_m^{ig}\right) \quad (20)$$

$$G_m^l = G_m^{ig} + \left(G_m^l - G_m^{ig}\right) \quad (21)$$

$$S_m^v = S_m^{ig} + \left(S_m^v - S_m^{ig}\right) \quad (22)$$

$$S_m^l = S_m^{ig} + \left(S_m^l - S_m^{ig}\right) \quad (23)$$

Vapor and liquid volume is computed by solving $p(T,V_m)$ for V_m or computed by an empirical correlation.

Advantages and Disadvantages of the Equation-of-State Method

You can use equations of state over wide ranges of temperature and pressure, including subcritical and supercritical regions. For ideal or slightly non-ideal systems, thermodynamic properties for both the vapor and liquid phases can be computed with a minimum amount of component data. Equations of state are suitable for modeling hydrocarbon systems with light gases such as CO_2, N_2, and H_2S.

For the best representation of non-ideal systems, you must obtain binary interaction parameters from regression of experimental vapor-liquid equilibrium (VLE) data. Equation of state binary parameters for many component pairs are available in the Aspen Physical Property System.

The assumptions in the simpler equations of state (Redlich-Kwong-Soave, Peng-Robinson, Lee-Kesler-Plöcker) are not capable of representing highly non-ideal chemical systems, such as alcohol-water systems. Use the activity-coefficient options sets for these systems at low pressures. At high pressures, use the flexible and predictive equations of state.

Equations of state generally do a poor job at predicting liquid density. To compensate for this, PENG-ROB, LK-PLOCK, RK-SOAVE, and the methods based on these calculate liquid density using the API correlation for pseudocomponents and the Rackett model for real components, rather than using the liquid density predicted by the equation of state. This is more accurate, but using causes a minor inconsistency which is mainly apparent for supercritical fluids, where the vapor and liquid properties should be the same, but the density will not be. All other equation-of-state methods use the equation of state to calculate liquid density, except that SRK and some of the methods based on it correct this density with a volume translation term based on the Peneloux-Rauzy method.

Activity Coefficient Method

In an ideal liquid solution, the liquid fugacity of each component in the mixture is directly proportional to the mole fraction of the component.

$$f_i^l = x_i f_i^{*,l} \tag{24}$$

The ideal solution assumes that all molecules in the liquid solution are identical in size and are randomly distributed. This assumption is valid for mixtures containing molecules of similar size and character. An example is a mixture of pentane (n-pentane) and 2,2-dimethylpropane (neopentane) (Gmehling et al., 1980, pp. 95-99). For this mixture, the molecules are of similar size and the intermolecular interactions between different component molecules are small (as for all nonpolar systems). Ideality can also exist between polar molecules, if the interactions cancel out. An example is the system water and 1,2-ethanediol (ethylene glycol) at 363 K (Gmehling et al., 1988, p. 124).

In general, you can expect non-ideality in mixtures of unlike molecules. Either the size and shape or the intermolecular interactions between components may be dissimilar. For short these are called size and energy asymmetry. Energy asymmetry occurs between polar and non-polar molecules and also between different polar molecules. An example is a mixture of alcohol and water.

The activity coefficient γ_i represents the deviation of the mixture from ideality (as defined by the ideal solution):

$$f_i^l = x_i \gamma_i f_i^{*,l} \tag{25}$$

The greater γ_i deviates from unity, the more non-ideal the mixture. For a pure component $x_i = 1$ and $\gamma_i = 1$, so by this definition a pure component is ideal. A mixture that behaves as the sum of its pure components is also defined as ideal (compare equation 24). This definition of ideality, relative to the pure liquid, is totally different from the definition of the ideality of an ideal gas, which has an absolute meaning (see Equation-of-State Method). These forms of ideality can be used next to each other.

In the majority of mixtures, γ_i is greater than unity. The result is a higher fugacity than ideal (compare equation 25 to equation 24). The fugacity can be interpreted as the tendency to vaporize. If compounds vaporize more than in an ideal solution, then they increase their average distance. So activity coefficients greater than unity indicate repulsion between unlike molecules. If the repulsion is strong, liquid-liquid separation occurs. This is another mechanism that decreases close contact between unlike molecules.

It is less common that γ_i is smaller than unity. Using the same reasoning, this can be interpreted as strong attraction between unlike molecules. In this case, liquid-liquid separation does not occur. Instead formation of complexes is possible.

Vapor-Liquid Equilibria (Activity Coefficient Methods)

In the activity coefficient approach, the basic vapor-liquid equilibrium relationship is represented by:

$$\varphi_i^v y_i p = x_i \gamma_i f_i^{*,l} \tag{26}$$

The vapor phase fugacity coefficient φ_i^v is computed from an equation of state (see Equation-of-State Method). The liquid activity coefficient γ_i is computed from an activity coefficient model.

For an ideal gas, $\varphi_i^v = 1$. For an ideal liquid, $\gamma_i = 1$. Combining this with equation 26 gives Raoult's law:

$$y_i p = x_i p_i^{*,l} \tag{27}$$

At low to moderate pressures, the main difference between equations 26 and 27 is due to the activity coefficient. If the activity coefficient is larger than unity, the system is said to show positive deviations from Raoults law. Negative deviations from Raoult's law occur when the activity coefficient is smaller than unity.

Liquid Phase Reference Fugacity

The liquid phase reference fugacity $f_i^{*,l}$ from equation 26 can be computed in three ways:

For solvents: The reference state for a solvent is defined as pure component in the liquid state, at the temperature and pressure of the system. By definition γ_i approaches unity as x_i approaches unity.

The liquid phase reference fugacity $f_i^{*,l}$ is computed as:

$$f_i^{*,l} = \varphi_i^{*,v}(T, p_i^{*,l})\, p_i^{*,l} \theta_i^{*,l} \tag{28}$$

Where:

$\varphi_i^{*,v}$ = Fugacity coefficient of pure component *i* at the system temperature and vapor pressures, as calculated from the vapor phase equation of state

$p_i^{*,l}$ = Liquid vapor pressures of component *i* at the system temperature

$\theta_i^{*,l}$ = Poynting correction for pressure

$$= \exp\left(\frac{1}{RT}\int_{p_i^{*,l}}^{p} V_i^{*,l}\, dp\right)$$

At low pressures, the Poynting correction is near unity, and can be ignored.

For dissolved gases: Light gases (such as O_2 and N_2) are usually supercritical at the temperature and pressure of the solution. In that case pure component vapor pressure is meaningless and therefore it cannot serve as the reference fugacity. The reference state for a dissolved gas is redefined to be at infinite dilution and at the temperature and pressure of the mixtures. The liquid phase reference fugacity $f_i^{*,l}$ becomes H_i (the Henry's constant for component i in the mixture).

The activity coefficient γ_i is converted to the infinite dilution reference state through the relationship:

$$\gamma^* = \left(\gamma_i / \gamma_i^\infty\right) \tag{29}$$

Where:

γ_i^∞ = The infinite dilution activity coefficient of component i in the mixture

By this definition γ^* approaches unity as x_i approaches zero. The phase equilibrium relationship for dissolved gases becomes:

$$\varphi_i^v y_i p = x_i \gamma_i^* H_i \tag{30}$$

To compute H_i, you must supply the Henry's constant for the dissolved-gas component i in each subcritical solvent component.

Using an Empirical Correlation: The reference state fugacity is calculated using an empirical correlation. Examples are the Chao-Seader or the Grayson-Streed model.

Electrolyte and Multicomponent VLE

The vapor-liquid equilibrium equations 26 and 30, only apply for components which occur in both phases. Ions are components which do not participate directly in vapor-liquid equilibrium. This is true as well for solids which do not dissolve or vaporize. However, ions influence activity coefficients of the other species by interactions. As a result they participate indirectly in the vapor-liquid equilibria. An example is the lowering of the vapor pressure of a solution upon addition of an electrolyte. For more on electrolyte activity coefficient models, see Activity Coefficient Models.

Multicomponent vapor-liquid equilibria are calculated from binary parameters. These parameters are usually fitted to binary phase equilibrium data (and not multicomponent data) and represent therefore binary information. The prediction of multicomponent phase behavior from binary information is generally good.

Liquid-Liquid and Liquid-Liquid-Vapor Equilibria (Activity Coefficient Method)

The basic liquid-liquid-vapor equilibrium relationship is:

$$x_i^{l1}\gamma_i^{l1}f_i^{*,l} = x_i^{l2}\gamma_i^{l2}f_i^{*,l} = \varphi_i^v y_i p \tag{31}$$

Equation 31 can be derived from the liquid-vapor equilibrium relationship by analogy. For liquid-liquid equilibria, the vapor phase term can be omitted, and the pure component liquid fugacity cancels out:

$$x_i^{l1}\gamma_i^{l1} = x_i^{l2}\gamma_i^{l2} \tag{32}$$

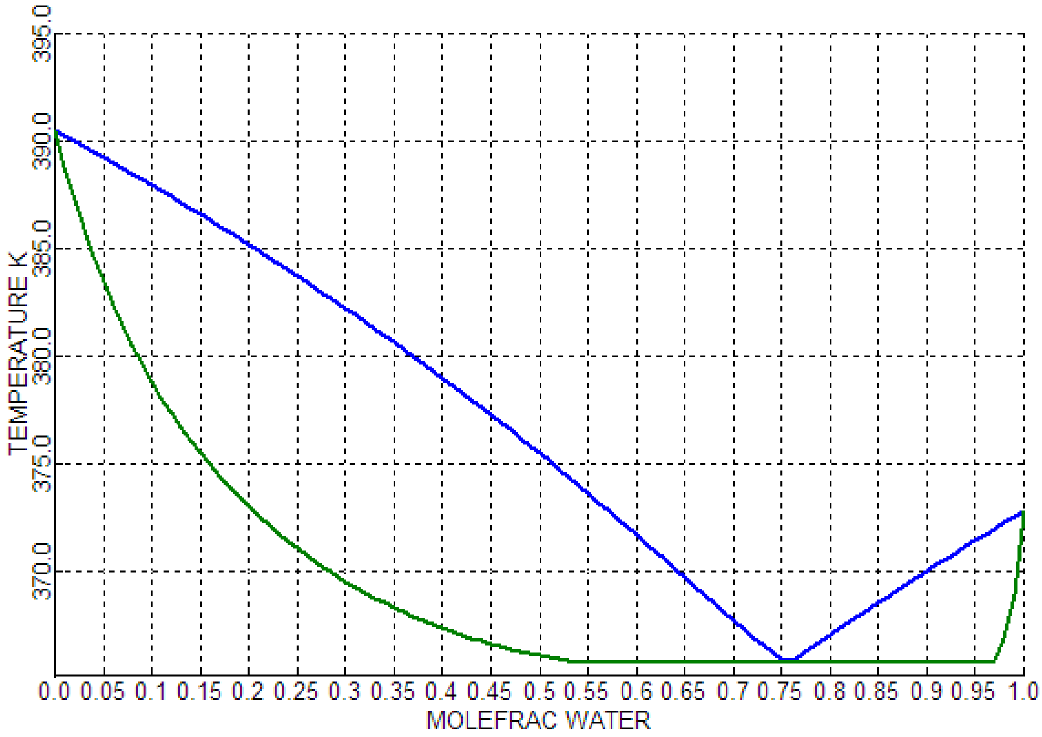
The activity coefficients depend on temperature, and so do liquid-liquid equilibria. However, equation 32 is independent of pressure. The activity coefficient method is very well suited for liquid-liquid equilibria at low to moderate pressures. Mutual solubilities do not change with pressure in this case. For high-pressure liquid-liquid equilibria, mutual solubilities become a function of pressure. In that case, use an equation-of-state method.

For the computation of the different terms in equations 31 and 32, see Vapor-Liquid Equilibria.

Multi-component liquid-liquid equilibria cannot be reliably predicted from binary interaction parameters fitted to binary data only. In general, regression of binary parameters from multi-component data will be necessary. See Regressing Property Data in the help for details.

The ability of activity coefficient models in describing experimental liquid-liquid equilibria differs. The Wilson model cannot describe liquid-liquid separation at all; UNIQUAC, UNIFAC and NRTL are suitable. For details, see Activity Coefficient Models. Activity coefficient models sometimes show anomalous behavior in the metastable and unstable composition region. Phase equilibrium calculation using the equality of fugacities of all components in all phases (as in equations 31 and 32), can lead to unstable solutions. Instead, phase equilibrium calculation using the minimization of Gibbs energy always yields stable solutions.

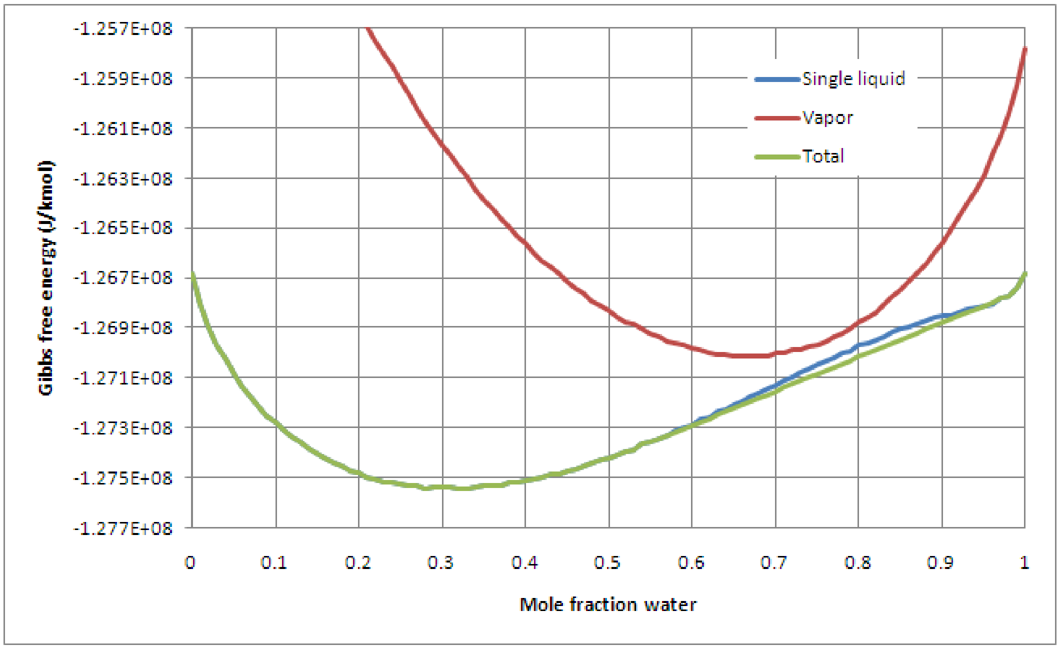
The figure labeled (T,x,x,y)—Diagram of Water and Butanol-1 at 1.01325 bar, a graphical Gibbs energy minimization of the system n-butanol + water, shows this.



(T,x,x,y)—Diagram of Water and Butanol-1 at 1.01325 bar

The phase diagram of n-butanol + water at 1 bar is shown in this figure. There is liquid-liquid separation below 367 K and there are vapor-liquid equilibria above this temperature. The diagram is calculated using the UNIFAC activity coefficient model with the liquid-liquid data set.

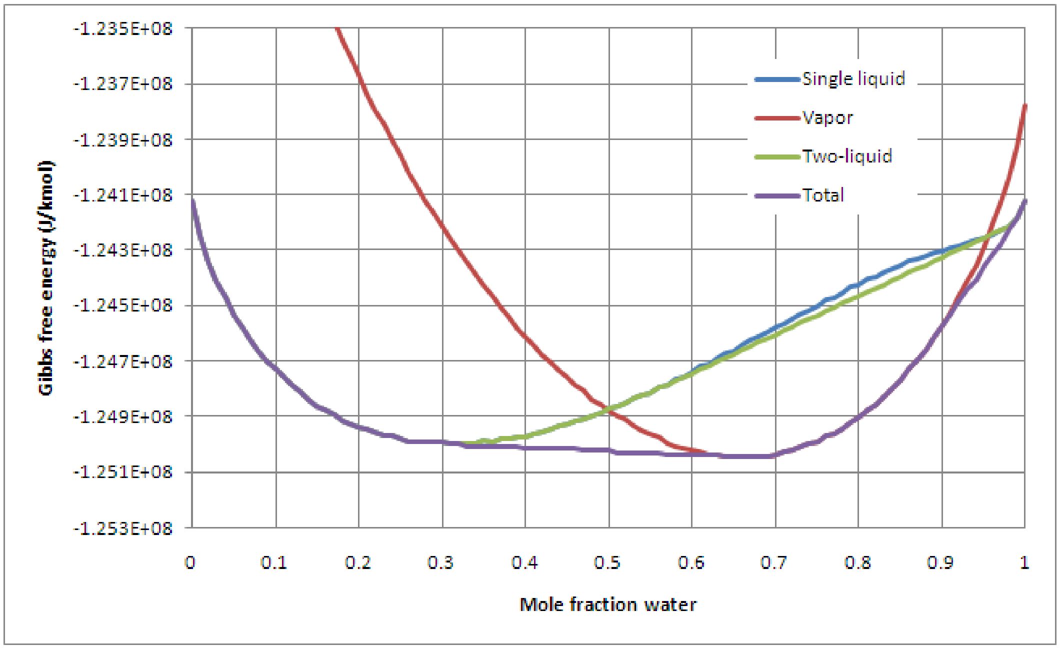
The Gibbs energies† of vapor and liquid phases at 1 bar and 365 K are given in the figure labeled Molar Gibbs Energy of Butanol-1 and Water at 365 K and 1 atm. This corresponds to a section of the phase diagram at 365 K. The Gibbs energy of the vapor phase is higher than that of the liquid phase at any mole fraction. This means that the vapor is unstable with respect to the liquid at these conditions. The minimum Gibbs energy of the system as a function of the mole fraction can be found graphically by stretching an imaginary string from below around the Gibbs curves. For the case of the figure labeled Molar Gibbs Energy of Butanol-1 and Water at 365 K and 1 atm, the string never touches the vapor Gibbs energy curve. For the liquid the situation is more subtle: the string touches the curve at the extremities but not at mole fractions between 0.56 and 0.97. In that range the string forms a double tangent to the curve. A hypothetical liquid mixture with mole fraction of 0.8 has a higher Gibbs energy and is unstable with respect to two liquid phases with mole fractions corresponding to the points where the tangent and the curve touch. The overall Gibbs energy of these two phases is a linear combination of their individual Gibbs energies and is found on the tangent (on the string). The mole fractions of the two liquid phases found by graphical Gibbs energy minimization are also indicated in the figure labeled (T,x,x,y)—Diagram of Water and Butanol-1 at 1.01325 bar.



Molar Gibbs Energy of Butanol-1 and Water at 365 K and 1 atm

† The Gibbs energy has been transformed by a contribution linear in the mole fraction, such that the Gibbs energy of pure liquid water (thermodynamic potential of water) has been shifted to the value of pure liquid n-butanol. This is done to make the Gibbs energy minimization visible on the scale of the graph. This transformation has no influence on the result of Gibbs energy minimization (Oonk, 1981).

At a temperature of 370 K, the vapor has become stable in the mole fraction range of 0.67 to 0.90 (see the figure labeled Molar Gibbs Energy of Butanol-1 and Water at 370 K and 1 atm). Graphical Gibbs energy minimization results in two vapor-liquid equilibria, indicated in the figure labeled Molar Gibbs Energy of Butanol-1 and Water at 370 K and 1 atm. Ignoring the Gibbs energy of the vapor and using a double tangent to the liquid Gibbs energy curve a liquid-liquid equilibrium is found. This is unstable with respect to the vapor-liquid equilibria. This unstable equilibrium will not be found with Gibbs minimization (unless the vapor is ignored) but can easily be found with the method of equality of fugacities.



Molar Gibbs Energy of Butanol-1 and Water at 370 K and 1 atm

The technique of Gibbs energy minimization can be used for any number of phases and components, and gives accurate results when handled by a computer algorithm. This technique is always used in the equilibrium reactor unit operation model RGibbs, and can be used optionally for liquid phase separation in the distillation model RadFrac.

Phase Equilibria Involving Solids

In most instances, solids are treated as inert with respect to phase equilibrium (CISOLID). This is useful if the components do not dissolve or vaporize. An example is sand in a water stream. CISOLID components may be stored in separate substreams or in the MIXED substream.

There are two areas of application where phase equilibrium involving solids may occur:

- Salt precipitation in electrolyte solutions
- Pyrometallurgical applications

Salt Precipitation

Electrolytes in solution often have a solid solubility limit. Solid solubilities can be calculated if the activity coefficients of the species and the solubility product are known (for details, see Electrolyte Calculation). The activity of the ionic species can be computed from an electrolyte activity coefficient model (see Activity Coefficient Models). The solubility product can be computed from the Gibbs energies of formation of the species participating in the precipitation reaction or can be entered as the temperature function (K-SALT) on the **Chemistry | Equilibrium Constants** sheet.

Salt precipitation is only calculated when the component is declared as a Salt on the **Chemistry | Stoichiometry** sheet. The salt components are part of the MIXED substream, because they participate in phase equilibrium. The types of equilibria are liquid-solid or vapor-liquid-solid. Each precipitating salt is treated as a separate, pure component, solid phase.

Solid compounds, which are composed of stoichiometric amounts of other components, are treated as pure components. Examples are salts with crystal water, like $CaSO_4$, H_2O.

Phase Equilibria Involving Solids for Metallurgical Applications

Mineral and metallic solids can undergo phase equilibria in a similar way as organic liquids. Typical pyrometallurgical applications have specific characteristics:

- Simultaneous occurrence of multiple solid and liquid phases
- Occurrence of simultaneous phase and chemical equilibria
- Occurrence of mixed crystals or solid solutions

These specific characteristics are incompatible with the chemical and phase equilibrium calculations by flash algorithms as used for chemical and petrochemical applications. Instead, these equilibria can be calculated by using Gibbs energy minimization techniques. In Aspen Plus, the unit operation model RGibbs is specially designed for this purpose.

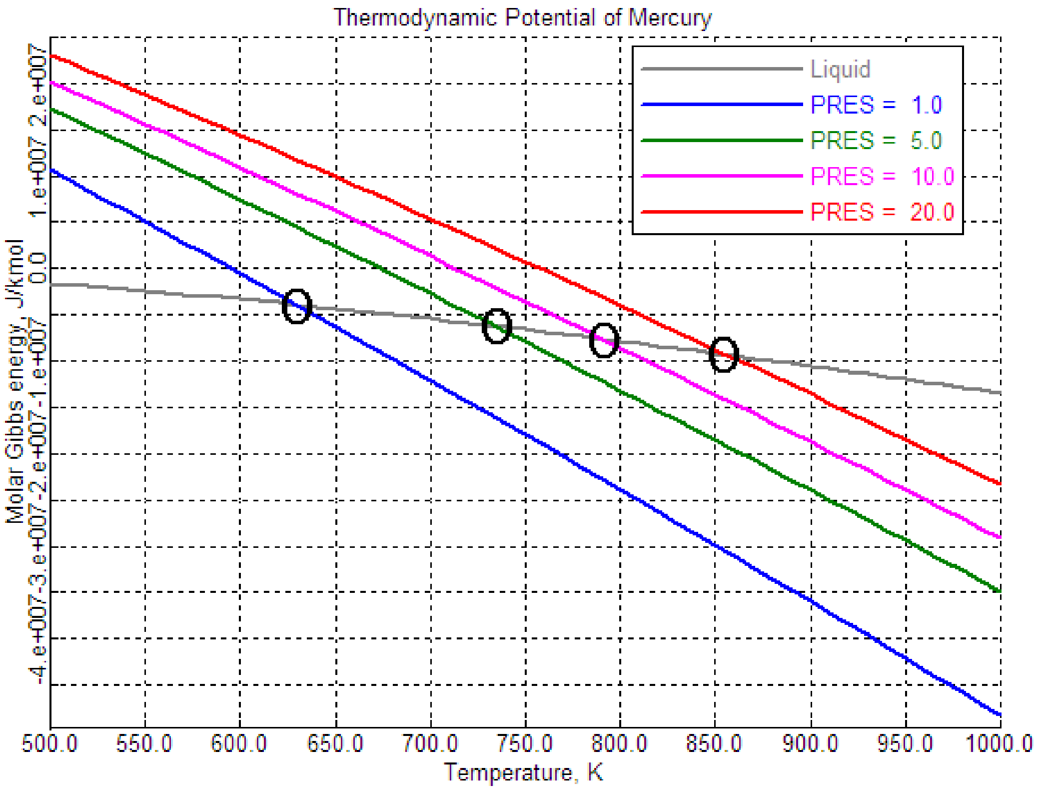
Gibbs energy minimization techniques are equivalent to phase equilibrium computations based on equality of fugacities. If the distribution of the components of a system is found, such that the Gibbs energy is minimal, equilibrium is obtained. (Compare the discussion of phase equilibrium calculation using Gibbs energy minimization in Liquid-Liquid and Liquid-Liquid-Vapor Equilibria)

As a result, the analog of equation 31 holds:

$$x_i^{l1}\gamma_i^{l1}f_i^{*,l} = x_i^{l2}\gamma_i^{l2}f_i^{*,l} = \ldots x_i^{s1}\gamma_i^{s1}f_i^{*,s} = x_i^{s2}\gamma_i^{s2}f_i^{*,s} = \ldots\varphi_i^{v}y_ip \qquad (33)$$

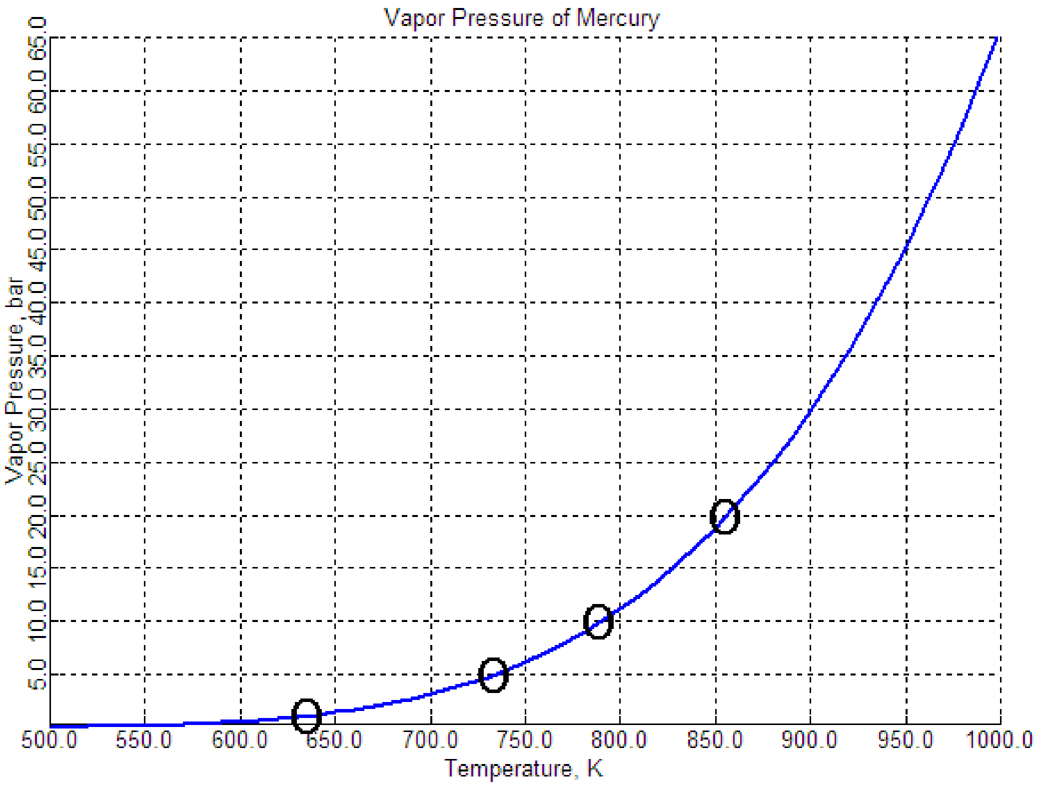
This equation can be simplified for pure component solids and liquids, or be extended for any number of phases.

For example, the pure component vapor pressure (or sublimation) curve can be calculated from the pure component Gibbs energies of vapor and liquid (or solid). The figure labeled Thermodynamic Potential of Mercury at 1, 5, 10, and 20 bar shows the pure component molar Gibbs energy or thermodynamic potential of liquid and vapor mercury as a function of temperature and at four different pressures: 1,5,10 and 20 bar†. The thermodynamic potential of the liquid is not dependent on temperature and independent of pressure: the four curves coincide. The vapor thermodynamic potential is clearly different at each pressure. The intersection point of the liquid and vapor thermodynamic potentials at 1 bar is at about 630 K. At this point the thermodynamic potentials of the two phases are equal, so there is equilibrium. A point of the vapor pressure curve is found. Below this temperature the liquid has the lower thermodynamic potential and is the stable phase; above this temperature the vapor has the lower thermodynamic potential. Repeating the procedure for all four pressures gives the four points indicated on the vapor pressure curve (see the figure labeled Vapor Pressure Curve of Liquid Mercury). This is a similar result as a direct calculation with the Antoine equation. The procedure can be repeated for a large number of pressures to construct the curve with sufficient accuracy. The sublimation curve can also be calculated using an Antoine type model, similar to the vapor pressure curve of a liquid.



Thermodynamic Potential of Mercury at 1, 5, 10, and 20 bar

†The pure component molar Gibbs energy is equal to the pure component thermodynamic potential. The ISO and IUPAC recommendation to use the thermodynamic potential is followed.



Vapor Pressure Curve of Liquid Mercury

The majority of solid databank components occur in the INORGANIC databank. In that case, pure component Gibbs energy, enthalpy and entropy of solid, liquid or vapor are calculated by polynomials (see *Physical Property Models*).

The pure component solid properties (Gibbs energy and enthalpy) together with the liquid and vapor mixture properties are sufficient input to calculate chemical and phase equilibria involving pure solid phases. In some cases mixed crystals or solid solutions can occur. These are separate phases. The concept of ideality and nonideality of solid solutions are similar to those of liquid phases (see Vapor-Liquid Equilibria). The activity coefficient models used to describe nonideality of the solid phase are different than those generally used for liquid phases. However some of the models (Margules, Redlich-Kister) can be used for liquids as well. If multiple liquid and solid mixture phases occur simultaneously, the activity coefficient models used can differ from phase to phase.

To be able to distinguish pure component solids from solid solutions in the stream summary, the pure component solids are placed in the CISOLID substream and the solid solutions in the MIXED substream, when the CISOLID substream exists.

Calculation of Other Properties Using Activity Coefficients

Properties can be calculated for vapor, liquid or solid phases:

Vapor phase: Vapor enthalpy, entropy, Gibbs energy and density are computed from an equation of state (see Calculation of Properties Using an Equation-of-State Property Method).

Liquid phase: Liquid mixture enthalpy is computed as:

$$H_m^l = \sum_i x_i \left(H_i^{*,v} - \Delta_{vap} H_i^* \right) + H_m^{E,l} \tag{34}$$

Where:

$H_i^{*,v}$ = Pure component vapor enthalpy at T and vapor pressure

$\Delta_{vap} H_i^*$ = Component vaporization enthalpy

$H_m^{E,l}$ = Excess liquid enthalpy

Excess liquid enthalpy $H_m^{E,l}$ is related to the activity coefficient through the expression:

$$H_m^{E,l} = -RT^2 \sum_i x_i \frac{\partial \ln \gamma_i}{\partial T} \tag{35}$$

Liquid mixture Gibbs free energy and entropy are computed as:

$$S_m^l = \tfrac{1}{T} \left(H_m^l - G_m^l \right) \tag{36}$$

$$G_m^l = G_m^v - RT \sum_i \ln \varphi_i^{*,l} + G_m^{E,l} \tag{37}$$

Where:

$$G_m^{E,l} = RT \sum_i x_i \ln \gamma_i \tag{38}$$

Liquid density is computed using an empirical correlation.

Solid phase: Solid mixture enthalpy is computed as:

$$H_m^s = \sum_i x_i^s H_i^{*,s} + H_m^{E,s} \tag{39}$$

Where:

$H_i^{*,s}$ = Pure component solid enthalpy at T

$H_m^{E,s}$ = The excess solid enthalpy

Excess solid enthalpy $H_m^{E,s}$ is related to the activity coefficient through the expression:

$$H_m^{E,s} = -RT^2 \sum_i x_i \frac{\partial \ln \gamma_i}{\partial T} \tag{40}$$

Solid mixture Gibbs energy is computed as:

$$G_m^s = \sum_i x_i \mu_i^{*,s} + G_m^{E,s} + RT \sum_i x_i^s \ln x_i^s \tag{41}$$

Where:

$$G_m^{E,s} = RT \sum_i x_i^s \ln \gamma_i^s \tag{42}$$

The solid mixture entropy follows from the Gibbs energy and enthalpy:

$$S_m^s = \tfrac{1}{T}(H_m^s - G_m^s) \tag{43}$$

Advantages and Disadvantages of the Activity Coefficient Method

The activity coefficient method is the best way to represent highly non-ideal liquid mixtures at low pressures. You must estimate or obtain binary parameters from experimental data, such as phase equilibrium data. Binary parameters for the Wilson, NRTL, and UNIQUAC models are available in the Aspen Physical Property System for a large number of component pairs. These binary parameters are used automatically. See Binary Parameters for Activity Coefficient Models in Physical Property Data in the help, for details.

Binary parameters are valid only over the temperature and pressure ranges of the data. Binary parameters outside the valid range should be used with caution, especially in liquid-liquid equilibrium applications. If no parameters are available, the predictive UNIFAC models can be used.

The activity coefficient approach should be used only at low pressures (below 10 atm). For systems containing dissolved gases at low pressures and at small concentrations, use Henry's law. For highly non-ideal chemical systems at high pressures, use the flexible and predictive equations of state.

Equation-of-State Models

The simplest equation of state is the ideal gas law:

$$p = RT / V_m \tag{44}$$

The ideal gas law assumes that molecules have no size and that there are no intermolecular interactions. This can be called absolute ideality, in contrast to ideality defined relative to pure component behavior, as used in the activity coefficient approach (see Activity Coefficient Method).

There are two main types of engineering equations of state: cubic equations of state and the virial equations of state. Steam tables are an example of another type of equation of state.

Cubic Equations of State

In an ideal gas, molecules have no size and therefore no repulsion. To correct the ideal gas law for repulsion, the total volume must be corrected for the volume of the molecule(s), or covolume *b*. (Compare the first term of equation 45 to equation 44. The covolume can be interpreted as the molar volume at closest packing.

The attraction must decrease the total pressure compared to an ideal gas, so a negative term is added, proportional to an attraction parameter *a*. This term is divided by an expression with dimension m^3, because attractive forces are proportional to r^{-6}, with *r* being the distance between molecules.

An example of this class of equations is the Soave-Redlich-Kwong equation of state (Soave, 1972):

$$p = \frac{RT}{(V_m - b)} - \frac{a(T)}{V_m(V_m + b)} \qquad (45)$$

Equation 45 can be written as a cubic polynomial in V_m. With the two terms of equation 45 and using simple mixing rules (see Mixtures, below). the Soave-Redlich-Kwong equation of state can represent non-ideality due to compressibility effects. The Peng-Robinson equation of state (Peng and Robinson, 1976) is similar to the Soave-Redlich-Kwong equation of state. Since the publication of these equations, many improvements and modifications have been suggested. A selection of important modifications is available in the Aspen Physical Property System. The original Redlich-Kwong-Soave and Peng-Robinson equations will be called standard cubic equations of state. Cubic equations of state in the Aspen Physical Property System are based on the Redlich-Kwong-Soave and Peng-Robinson equations of state. Equations are listed in the following table.

Cubic Equations of State in the Aspen Physical Property System

Redlich-Kwong(-Soave) based	Peng-Robinson based
Redlich-Kwong	Standard Peng-Robinson

Redlich-Kwong(-Soave) based	**Peng-Robinson based**
Standard Redlich-Kwong-Soave	Peng-Robinson
Redlich-Kwong-Soave	Peng-Robinson-MHV2
Redlich-Kwong-ASPEN	Peng-Robinson-WS
Schwartzentruber-Renon	
Redlich-Kwong-Soave-MHV2	
Predictive SRK	
Redlich-Kwong-Soave-WS	

Pure Components

In a standard cubic equation of state, the pure component parameters are calculated from correlations based on critical temperature, critical pressure, and acentric factor. These correlations are not accurate for polar compounds or long chain hydrocarbons. Introducing a more flexible temperature dependency of the attraction parameter (the alpha-function), the quality of vapor pressure representation improves. Up to three different alpha functions are built-in to the following cubic equation-of-state models in the Aspen Physical Property System: Redlich-Kwong-Aspen, Schwartzenruber-Renon, Peng-Robinson-MHV2, Peng-Robinson-WS, Predictive RKS, Redlich-Kwong-Soave-MHV2, and Redlich-Kwong-Soave-WS.

Cubic equations of state do not represent liquid molar volume accurately. To correct this you can use volume translation, which is independent of VLE computation. The Schwartzenruber-Renon equation of state model has volume translation.

Mixtures

The cubic equation of state calculates the properties of a fluid as if it consisted of one (imaginary) component. If the fluid is a mixture, the parameters *a* and *b* of the imaginary component must be calculated from the pure component parameters of the real components, using mixing rules. The classical mixing rules, with one binary interaction parameter for the attraction parameter, are not sufficiently flexible to describe mixtures with strong shape and size asymmetry:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} \left(1 - k_{a,ij}\right) \tag{46}$$

$$b = \sum_i x_i b_i = \sum_i \sum_j x_i x_j \left(\frac{b_i + b_j}{2}\right) \tag{47}$$

A second interaction coefficient is added for the b parameter in the Redlich-Kwong-Aspen (Mathias, 1983) and Schwartzentruber-Renon (Schwartzentruber and Renon, 1989) equations of state:

$$b = \sum_i \sum_j x_i x_j \left(\frac{b_i + b_j}{2} \right) (1 - k_{b,ij}) \tag{48}$$

This is effective to fit vapor-liquid equilibrium data for systems with strong size and shape asymmetry but it has the disadvantage that $k_{b,ij}$ is strongly correlated with $k_{a,ij}$ and that $k_{b,ij}$ affects the excess molar volume (Lermite and Vidal, 1988).

For strong energy asymmetry, in mixtures of polar and non-polar compounds, the interaction parameters should depend on composition to achieve the desired accuracy of representing VLE data. Huron-Vidal mixing rules use activity coefficient models as mole fraction functions (Huron and Vidal, 1979). These mixing rules are extremely successful in fitting because they combine the advantages of flexibility with a minimum of drawbacks (Lermite and Vidal, 1988). However, with the original Huron-Vidal approach it is not possible to use activity coefficient parameters, determined at low pressures, to predict the high pressure equation-of-state interactions.

Several modifications of Huron-Vidal mixing rules exist which use activity coefficient parameters obtained at low pressure directly in the mixing rules (see the table labeled Cubic Equations of State in the Aspen Physical Property System). They accurately predict binary interactions at high pressure. In practice this means that the large database of activity coefficient data at low pressures (DECHEMA Chemistry Data Series, Dortmund DataBank) is now extended to high pressures.

The MHV2 mixing rules (Dahl and Michelsen, 1990), use the Lyngby modified UNIFAC activity coefficient model (See Activity Coefficient Models). The quality of the VLE predictions is good.

The *Predictive SRK* method (Holderbaum and Gmehling, 1991; Fischer, 1993) uses the original UNIFAC model. The prediction of VLE is good. The mixing rules can be used with any equation of state, but it has been integrated with the Redlich-Kwong-Soave equation of state in the following way: new UNIFAC groups have been defined for gaseous components, such as hydrogen. Interaction parameters for the new groups have been regressed and added to the existing parameter matrix. This extends the existing low pressure activity coefficient data to high pressures, and adds prediction of gas solubilities at high pressures.

The Wong-Sandler mixing rules (Wong and Sandler, 1992; Orbey et al., 1993) predict VLE at high pressure equally well as the MHV2 mixing rules. Special attention has been paid to the theoretical correctness of the mixing rules at pressures approaching zero.

Virial Equations of State

Virial equations of state in the Aspen Physical Property System are:

- Hayden-O'Connell
- BWR-Lee-Starling
- Lee-Kesler-Plöcker

This type of equation of state is based on a selection of powers of the expansion:

$$p = RT\left(\frac{1}{V_m} + \frac{B}{V_m^2} + \frac{C}{V_m^3} + \ldots\right) \tag{49}$$

Truncation of equation 49 after the second term and the use of the second virial coefficient *B* can describe the behavior of gases up to several bar. The Hayden-O'Connell equation of state uses a complex computation of *B* to account for the association and chemical bonding in the vapor phase (see Vapor Phase Association).

Like cubic equations of state, some of these terms must be related to either repulsion or attraction. To describe liquid and vapor properties, higher order terms are needed. The order of the equations in V is usually higher than cubic. The Benedict-Webb-Rubin equation of state is a good example of this approach. It had many parameters generalized in terms of critical properties and acentric factor by Lee and Starling (Brulé et al., 1982). The Lee-Kesler-Plöcker equation of state is another example of this approach.

Virial equations of state for liquid and vapor are more flexible in describing a (*p,V*) isotherm because of the higher degree of the equation in the volume. They are more accurate than cubic equations of state. Generalizations have been focused mainly on hydrocarbons, therefore these compounds obtain excellent results. They are not recommended for polar compounds.

The standard mixing rules give good results for mixtures of hydrocarbons and light gases.

Vapor Phase Association

Nonpolar substances in the vapor phase at low pressures behave almost ideally. Polar substances can exhibit nonideal behavior or even association in the vapor phase. Association can be expected in systems with hydrogen bonding such as alcohols, aldehydes and carboxylic acids. Most hydrogen bonding leads to dimers. HF is an exception; it forms mainly hexamers. This section uses dimerization as an example to discuss the chemical theory used to describe strong association. Chemical theory can be used for any type of reaction.

If association occurs, chemical reactions take place. Therefore, a model based on physical forces is not sufficient. Some reasons are:

- Two monomer molecules form one dimer molecule, so the total number of species decreases. As a result the mole fractions change. This has influence on VLE and molar volume (density).
- The heat of reaction affects thermal properties like enthalpy, C_p.

The equilibrium constant of a dimerization reaction,

$$2A \leftrightarrow A_2 \tag{50}$$

in the vapor phase is defined in terms of fugacities:

$$K = \frac{f_{A_2}}{f_A^2} \tag{51}$$

With:

$$f_i^v = \varphi_i^v y_i p \tag{52}$$

and realizing that φ_i^v is approximately unity at low pressures:

$$K = \frac{y_{A_2}}{y_A^2 p} \tag{53}$$

Equations 51-53 are expressed in terms of true species properties. This may seem natural, but unless measurements are done, the true compositions are not known. On the contrary, the composition is usually given in terms of *unreacted* or apparent species (Abbott and van Ness, 1992), which represents the imaginary state of the system if no reaction takes place. Superscripts *t* and *a* are used to distinguish clearly between true and apparent species. (For more on the use of apparent and true species approach, see Apparent Component and True Component Approaches in Physical Property Methods).

K in equation 53 is only a function of temperature. If the pressure approaches zero at constant temperature, $\frac{y_{A_2}}{y_A^2}$,which is a measure of the degree of association, must decrease. It must go to zero for zero pressure where the ideal gas behavior is recovered. The degree of association can be considerable at atmospheric pressure: for example acetic acid at 293 K and 1 bar is dimerized at about 95% (Prausnitz et al., 1986).

The equilibrium constant is related to the thermodynamic properties of reaction:

$$\ln K = -\frac{\Delta_r G}{RT} = -\frac{\Delta_r H}{RT} + \frac{\Delta_r S}{R} \tag{54}$$

The Gibbs energy, the enthalpy, and the entropy of reaction can be approximated as independent of temperature. Then from equation 54 it follows that ln *K* plotted against 1/*T* is approximately a straight line with a positive slope (since the reaction is exothermic) with increasing 1/*T*. This represents a decrease of ln *K* with increasing temperature. From this it follows (using equation 53) that the degree of association decreases with increasing temperature.

It is convenient to calculate equilibria and to report mole fractions in terms of apparent components. The concentrations of the true species have to be calculated, but are not reported. Vapor-liquid equilibria in terms of apparent components require apparent fugacity coefficients.

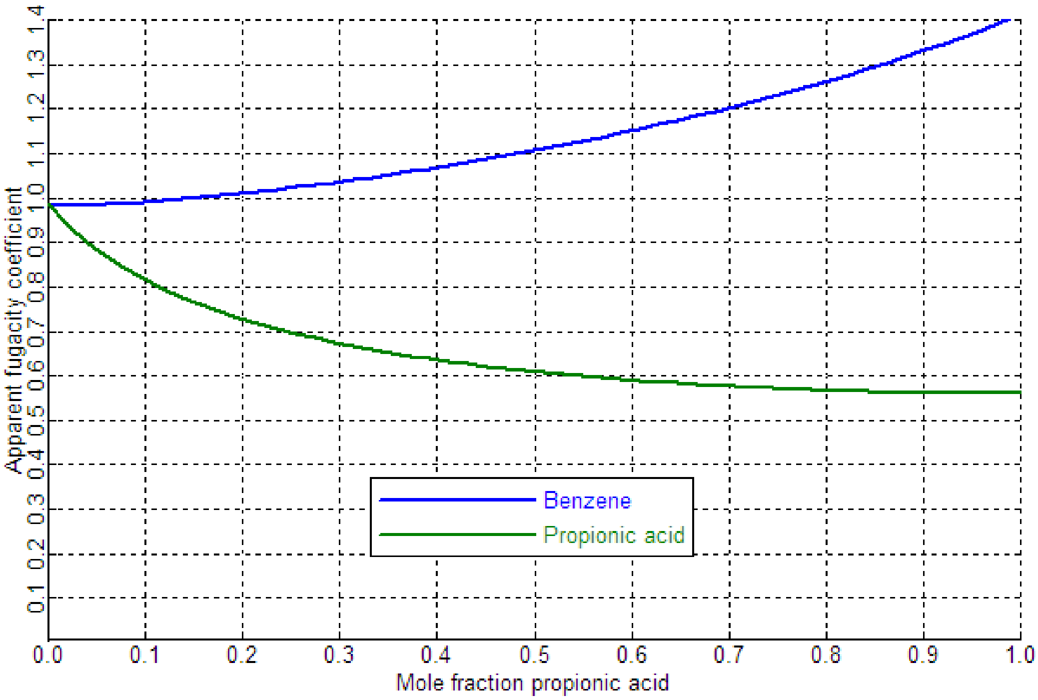
The fugacity coefficients of the true species are expected to be close to unity (ideal) at atmospheric pressure. However the apparent fugacity coefficient needs to reflect the decrease in apparent partial pressure caused by the decrease in number of species.

The apparent partial pressure is represented by the term $y_i^a p$ in the vapor fugacity equation applied to apparent components:

$$f_i^{a,v} = \varphi_i^{a,v} y_i^a p \tag{55}$$

In fact the apparent and true fugacity coefficients are directly related to each other by the change in number of components (Nothnagel et al., 1973; Abbott and van Ness, 1992):

$$\varphi_i^{a,v} = \varphi_i^{t,v} \frac{y_i^t}{y_i^a} \tag{56}$$



Apparent Fugacity of Vapor Benzene and Propionic Acid

This is why apparent fugacity coefficients of associating species are well below unity. This is illustrated in the figure labeled Apparent Fugacity of Vapor

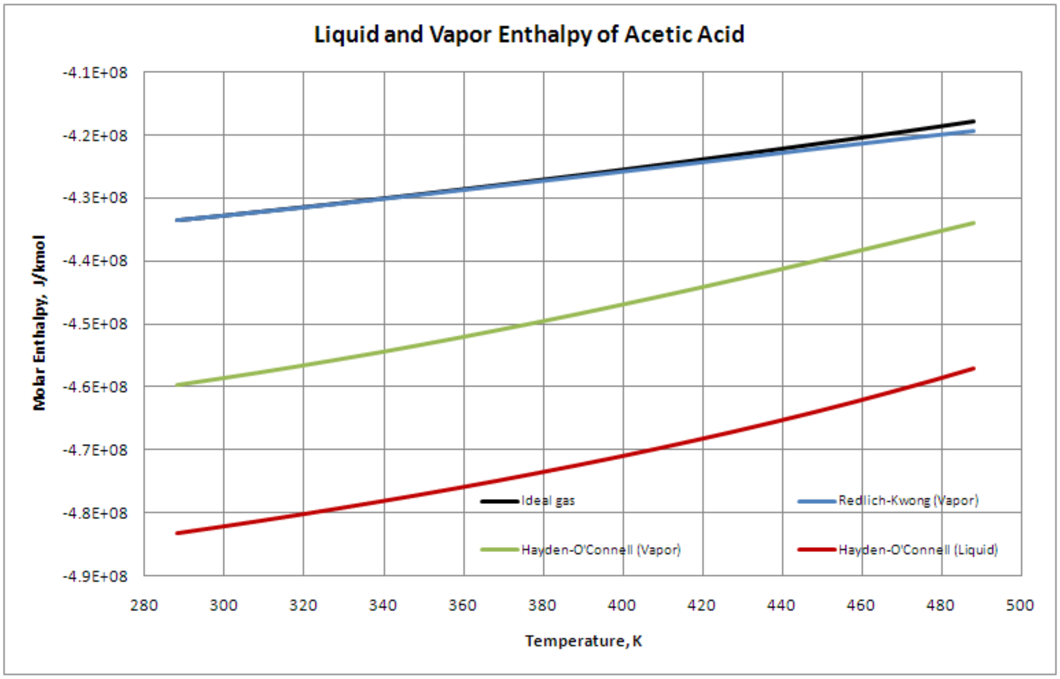
Benzene and Propionic Acid for the system benzene + propionic acid at 415 K and 101.325 kPa (1 atm) (Nothnagel et al., 1973). The effect of dimerization clearly decreases below apparent propionic acid mole fractions of about 0.2 (partial pressures of 20 kPa). The effect vanishes at partial pressures of zero, as expected from the pressure dependence of equation 53. The apparent fugacity coefficient of benzene increases with increasing propionic acid mole fraction. This is because the true mole fraction of propionic acid is higher than its apparent mole fraction (see equation 56).

The vapor enthalpy departure needs to be corrected for the heat of association. The true heat of association can be obtained from the equilibrium constant:

$$\Delta_r H_m^t = -T^2 \frac{d(\Delta_r G_m^t)}{dT} = RT^2 \frac{d(\ln K)}{dT} \qquad (57)$$

The value obtained from equation 57 must be corrected for the ratio of true to apparent number of species to be consistent with the apparent vapor enthalpy departure. With the enthalpy and Gibbs energy of association (equations 57 and 54), the entropy of association can be calculated.

The apparent heat of vaporization of associating components as a function of temperature can show a maximum. The increase of the heat of vaporization with temperature is probably related to the decrease of the degree of association with increasing temperature. However, the heat of vaporization must decrease to zero when the temperature approaches the critical temperature. The figure labeled Liquid and Vapor Enthalpy of Acetic Acid illustrates the enthalpic behavior of acetic acid. Note that the enthalpy effect due to association is very large.



Liquid and Vapor Enthalpy of Acetic Acid

The true molar volume of an associating component is close to the true molar volume of a non-associating component. At low pressures, where the ideal gas law is valid, the true molar volume is constant and equal to p/RT, independent of association. This means that associated molecules have a higher molecular mass than their monomers, but they behave as an ideal gas, just as their monomers. This also implies that the mass density of an associated gas is higher than that of a gas consisting of the monomers. The apparent molar volume is defined as the true total volume per apparent number of species. Since the number of apparent species is higher than the true number of species the apparent molar volume is clearly smaller than the true molar volume.

The chemical theory can be used with any equation of state to compute true fugacity coefficients. At low pressures, the ideal gas law can be used.

For dimerization, two approaches are commonly used: the Nothnagel and the Hayden-O'Connell equations of state. For HF hexamerization a dedicated equation of state is available in the Aspen Physical Property System.

Nothnagel et al. (1973) used a truncated van der Waals equation of state. They correlated the equilibrium constants with the covolume *b*, a polarity parameter *p* and the parameter *d*. *b* can be determined from group contribution methods (Bondi, 1968) (or a correlation of the critical temperature and pressure (as in the Aspen Physical Property System). *d* and *p* are adjustable parameters. Many values for *d* and *p* are available in the Nothnagel equation of state in the Aspen Physical Property System. Also correction terms for the heats of association of unlike molecules are built-in. The equilibrium constant, *K*, has been correlated to T_b, T_c, *b*, *d*, and *p*.

Hayden and O'Connell (1975) used the Virial equation of state (equation 49), truncated after the second term. They developed a correlation for the second virial coefficient of polar, nonpolar and associating species based on the critical temperature and pressure, the dipole moment and the mean radius of gyration. Association of like and unlike molecules is described with the adjustable parameter η. Pure component and binary values for η are available in the Aspen Physical Property System.

The HF equation of state (de Leeuw and Watanasiri, 1993) assumes the formation of hexamers only. The fugacities of the true species are assumed to be ideal, and is therefore suited for low pressures. Special attention has been paid to the robustness of the algorithm, and the consistency of the results with theory. The equation of state has been integrated with the electrolyte NRTL activity coefficient model to allow the rigorous representation of absorption and stripping of HF with water. It can be used with other activity coefficient models for hydrocarbon + HF mixtures.

Activity Coefficient Models

This section discusses the characteristics of activity coefficient models. The description is divided into the following categories:

- Molecular models (correlative models for non-electrolyte solutions)
- Group contribution models (predictive models for non-electrolyte solutions)
- Electrolyte activity coefficient models

Molecular Models

The early activity coefficient models such as van Laar and Scatchard-Hildebrand, are based on the same assumptions and principles of regular solutions. Excess entropy and excess molar volume are assumed to be zero, and for unlike interactions, London's geometric mean rule is used. Binary parameters were estimated from pure component properties. The van Laar model is only useful as correlative model. The Scatchard-Hildebrand can predict interactions from solubility parameters for non-polar mixtures. Both models predict only positive deviations from Raoult's law (see Activity Coefficient Method).

The three-suffix Margules and the Redlich-Kister activity coefficient models are flexible arithmetic expressions.

Local composition models are very flexible, and the parameters have much more physical significance. These models assume ordering of the liquid solution, according to the interaction energies between different molecules. The Wilson model is suited for many types of non-ideality but cannot model liquid-liquid separation. The NRTL and UNIQUAC models can be used to describe VLE, LLE and enthalpic behavior of highly non-ideal systems. The WILSON, NRTL and UNIQUAC models are well accepted and are used on a regular basis to model highly non-ideal systems at low pressures.

A detailed discussion of molecular activity coefficient models and underlying theories can be found in Prausnitz et al. (1986).

Group Contribution Models

The UNIFAC activity coefficient model is an extension of the UNIQUAC model. It applies the same theory to functional groups that UNIQUAC uses for molecules. A limited number of functional groups is sufficient to form an infinite number of different molecules. The number of possible interactions between groups is very small compared to the number of possible interactions between components from a pure component database (500 to 2000 components). Group-group interactions determined from a limited, well chosen set of experimental data are sufficient to predict activity coefficients between almost any pair of components.

UNIFAC (Fredenslund et al., 1975; 1977) can be used to predict activity coefficients for VLE. For LLE a different dataset must be used. Mixture enthalpies, derived from the activity coefficients (see Activity Coefficient Method) are not accurate.

UNIFAC has been modified at the Technical University of Lyngby (Denmark). The modification includes an improved combinatorial term for entropy and the group-group interaction has been made temperature dependent. The three UNIFAC models are available in the Aspen Physical Property System. For detailed information on each model, see *Physical Property Models*.

This model can be applied to VLE, LLE and enthalpies (Larsen et al., 1987). Another UNIFAC modification comes from the University of Dortmund (Germany). This modification is similar to Lyngby modified UNIFAC, but it can also predict activity coefficients at infinite dilution (Weidlich and Gmehling, 1987).

Electrolyte Models

In electrolyte solutions a larger variety of interactions and phenomena exist than in non-electrolyte solutions. Besides physical and chemical molecule-molecule interactions, ionic reactions and interactions occur (molecule-ion and ion-ion). Electrolyte activity coefficient models (Electrolyte NRTL, Pitzer) are therefore more complicated than non-electrolyte activity coefficient models. Electrolytes dissociate so a few components can form many species in a solution. This causes a multitude of interactions, some of which are strong. This section gives a summary of the capabilities of the electrolyte activity coefficient models in the Aspen Physical Property System. For details, see *Physical Property Models*.

The Pitzer electrolyte activity coefficient model can be used for the representation of aqueous electrolyte solutions up to 6 molal strength (literature references: Chen et al., 1979; Fürst and Renon, 1982; Guggenheim, 1935; Guggenheim and Turgeon, 1955; Renon, 1981). The model handles gas solubilities. Excellent results can be obtained, but many parameters are needed.

The Electrolyte NRTL model is an extension of the molecular NRTL model (literature references: Chen et al., 1982; Chen and Evans, 1986; CRC Handbook, 1975; Mock et al., 1984, 1986; Renon and Prausnitz, 1968). It can handle electrolyte solutions of any strength, and is suited for solutions with multiple solvents, and dissolved gases. The flexibility of this model makes it very suitable for any low-to-moderate pressure application.

Electrolyte parameter databanks and data packages for industrially important applications have been developed for both models (see *Physical Property Data*). If parameters are not available, use data regression, or the Bromley-Pitzer activity coefficient model.

The Bromley-Pitzer activity coefficient model is a simplification of the Pitzer model (literature references: Bromley, 1973; Fürst and Renon, 1982). A correlation is used to calculate the interaction parameters. The model is limited in accuracy, but predictive.

Transport Property Methods

The Aspen Physical Property System property methods can compute the following transport properties:

- Viscosity
- Thermal conductivity
- Diffusion coefficient
- Surface tension

Each pure component property is calculated either from an empirical equation or from a semi-empirical (theoretical) correlation. The coefficients for the empirical equation are determined from experimental data and are stored in the Aspen Physical Property System databank. The mixture properties are calculated using appropriate mixing rules. This section discusses the methods for transport property calculation. The properties that have the most in common in their behavior are viscosity and thermal conductivity. This is reflected in similar methods that exist for these properties and therefore they are discussed together.

Viscosity and Thermal Conductivity Methods

When the pressure approaches zero, viscosity and thermal conductivity are linear functions of temperature with a positive slope. At a given temperature, viscosity and thermal conductivity increase with increasing density (density increases for any fluid with increasing pressure).

Detailed molecular theories exist for gas phase viscosity and thermal conductivity at low pressures. Some of these can account for polarity. These low pressure properties are not exactly ideal gas properties because non-ideality is taken into account. Examples are the General Pure Component Vapor Viscosity and the Chung-Lee-Starling low pressure vapor viscosity models and the General Pure Component Vapor Thermal Conductivity low pressure vapor thermal conductivity model.

Residual property models are available to account for pressure or density effects. These models calculate the difference of a certain property with respect to the low pressure value. The method used is:

$$x(p) = x(p = 0) + (x(p) - x(p = 0)) \tag{58}$$

Where:

x = Viscosity or thermal conductivity

Most of the low pressure models require mixing rules for calculating mixture properties.

Another class of models calculate the high pressure property directly from molecular parameters and state variables. For example the TRAPP models for hydrocarbons use critical parameters and acentric factor as molecular parameters. The models use temperature and pressure as state variables.

The Chung-Lee-Starling models use critical parameters, acentric factor, and dipole moment as molecular parameters. The models use temperature and density as state variables. These models generally use mixing rules for molecular parameters, rather than mixing rules for pure component properties.

Vapor viscosity, thermal conductivity, and vapor diffusivity are interrelated by molecular theories. Many thermal conductivity methods therefore require low pressure vapor viscosity either in calculating thermal conductivity or in the mixing rules.

Liquid properties are often described by empirical, correlative models, the General Pure Component models for liquid viscosity and thermal conductivity. These are accurate in the temperature and pressure ranges of the experimental data used in the fit. Mixing rules for these properties do not provide a good description for the excess properties.

Corresponding-states models such as Chung-Lee-Starling and TRAPP can describe both liquid and vapor properties. These models are more predictive and less accurate than a correlative model, but extrapolate well with temperature and pressure. Chung-Lee-Starling allows the use of binary interaction parameters and an association parameter, which can be adjusted to experimental data.

Diffusion Coefficient Methods (Theory)

It is evident that diffusion is related to viscosity, so several diffusion coefficient methods, require viscosity, for both liquid and for vapor diffusion coefficients. (Chapman-Enskog-Wilke-Lee and Wilke-Chang models).

Vapor diffusion coefficients can be calculated from molecular theories similar to those discussed for low pressure vapor viscosity and thermal conductivity. Similarly, pressure correction methods exist. The Dawson-Khoury-Kobayashi model calculates a pressure correction factor which requires the density as input.

Liquid diffusion coefficients depend on activity and liquid viscosity.

Binary diffusion coefficients are required in processes where mass transfer is limited. Binary diffusion coefficients describe the diffusion of one component at infinite dilution in another component. In multicomponent systems this corresponds to a matrix of values.

The average diffusion coefficient of a component in a mixture does not have any quantitative applications; it is an informative property. It is computed using a mixing rule for vapor diffusion coefficients and using mixture input parameters for the Wilke-Chang model.

Surface Tension Methods (Theory)

Surface tension is calculated by empirical, correlative models such as General Pure Component Liquid Surface Tension. An empirical linear mixing rule is used to compute mixture surface tension.

Nonconventional Component Enthalpy Calculation

Nonconventional components generally do not participate in phase equilibrium calculations, but are included in enthalpy balances. For a process unit in which no chemical change occurs, only sensible heat effects of nonconventional components are significant. In this case, the enthalpy reference state may be taken as the component at any arbitrary reference temperatures (for example, 298.15 K). If a nonconventional component is involved in a chemical reaction, an enthalpy balance is meaningful only if the enthalpy reference state is consistent with that adopted for conventional components: the constituents elements must be in their standard states at 1 atm and 298.15 K. (For example, for the standard state of carbon is solid (graphite), and the standard state of hydrogen, nitrogen, and chlorine is gaseous, all at 1 atm and 298.15 K. At these conditions, their heats of formation are zero.) The enthalpy is calculated as:

$$H^s = \Delta_f h^s + \int_{T^{ref}}^{T} C_p^s dT \quad (59)$$

Frequently the heat of formation $\Delta_f h^s$ is unknown and cannot be obtained directly because the molecular structure of the component is unknown. In many cases, it is possible to calculate the heat of formation from the heat of combustion $\Delta_c h^s$, because the combustion products and elemental composition of the components are known:

$$\Delta_f h^s = \Delta_c h^s + \Delta_f h_{cp}{}^s \quad (60)$$

$\Delta_f h_{cp}{}^s$ is the sum of the heats of formation of the combustion products multiplied by the mass fractions of the respective elements in the nonconventional component. This is the approach used in the coal enthalpy model HCOALGEN (see *Physical Property Models*). This approach is recommended for computing DHFGEN for the ENTHGEN model.

Enthalpy and heat capacity are available as property sets for non-conventional components.

Symbol Definitions

Roman Letters	Definitions
a	Equation of state energy parameter
b	Equation of state co-volume
B	Second virial coefficient
C_p	Heat capacity at constant pressure
C	Third virial coefficient
f	Fugacity
G	Gibbs energy
H	Henry's constant
H	Enthalpy
k	Equation of state binary parameter
K	Chemical equilibrium constant
n	Mole number
p	Pressure
R	Universal gas constant
S	Entropy
T	Temperature
V	Volume
x,y	Molefraction
Z	Compressibility factor

Greek Letters	Definitions
γ	Activity coefficient
θ	Poynting correction
φ	Fugacity coefficient
μ	Thermodynamic potential

Superscripts	Definitions
c	Combustion property
i	Component index
f	Formation property
m	Molar property
vap	Vaporization property
r	Reaction property
ref	Reference state property
*	Pure component property, asymmetric convention
∞	At infinite dilution
a	Apparent property
E	Excess property
ig	Ideal gas property
l	Liquid property
l2	Second liquid property
l1	First liquid property
s	Solid property
t	True property
v	Vapor property

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2 Property Method Descriptions

This chapter describes the Aspen Physical Property System property methods. Topics include:

- Classification of property methods (with lists of all property methods available in the Aspen Physical Property System)
- Recommended use
- Property method descriptions, organized by application

Since Aspen Physical Property System property methods are tailored to classes of compounds and operating conditions, they fit most engineering needs. Customization of property methods is explained in the Property Method Calculations and Routes chapter. Specific models are discussed in *Physical Property Models*.

Classification of Property Methods and Recommended Use

A property method is a collection of property calculation routes. (For more on routes, see Routes and Models). The properties involved are needed by unit operation models.

Thermodynamic properties:

- Fugacity coefficient (or equivalent: chemical potential, K-value)
- Enthalpy
- Entropy
- Gibbs energy
- Volume

Transport properties:

- Viscosity
- Thermal conductivity
- Diffusion coefficient
- Surface tension

Property methods allow you to specify a collection of property calculation procedures as one entity, for example, you might use them in a unit operation, or in a flowsheet (see Physical Property Methods in Using the Properties Environment in the help).

It is important to choose the right property method for an application to ensure the success of your calculation. To help you choose a property method, frequently encountered applications are listed with recommended property methods. (Multiple property methods often apply. A class of property methods is recommended, as opposed to an individual property method.)

The classes of property methods available are:

- IDEAL
- Reference correlations for specific components
- Liquid fugacity and K-value correlations
- Petroleum tuned equations of state
- Equations of state for high pressure hydrocarbon applications
- Flexible and predictive equations of state
- Liquid activity coefficients
- Electrolyte activity coefficients and correlations
- Solids processing
- Steam tables

After you have decided which property method class your application needs, refer to the corresponding section for more detailed recommendations. See *Physical Property Models* for detailed information on models and their parameter requirements. General usage issues, such as using Henry's law and the free-water approximation, are discussed in Physical Property Methods in Using the Properties Environment in the help.

Recommended Classes of Property Methods for Different Applications

Oil and Gas Production

Application	Recommended Property Method
Reservoir systems	Equations of state for high pressure hydrocarbon applications

Application	Recommended Property Method
Platform separation	Equations of state for high pressure hydrocarbon applications
Transportation of oil and gas by pipeline	Equations of state for high pressure hydrocarbon applications

Refinery

Application	Recommended Property Method
Low pressure applications(up to several atm) Vacuum tower Atmospheric crude tower	Petroleum fugacity and K-value correlations (and assay data analysis)
Medium pressure applications (up to several tens of atm) Coker main fractionator FCC main fractionator	Petroleum fugacity and K-value correlations Petroleum-tuned equations of state (and assay data analysis)
Hydrogen-rich applications Reformer Hydrofiner	Selected petroleum fugacity correlations Petroleum-tuned equations of state (and assay data analysis)
Lube oil unit De-asphalting unit	Petroleum-tuned equations of state (and assay data analysis)

Gas Processing

Application	Recommended Property Method
Hydrocarbon separations Demethanizer C3-splitter	Equations of state for high pressure hydrocarbon applications (with k_{ij})
Cryogenic gas processing Air separation	Equations of state for high pressure hydrocarbon applications Flexible and predictive equations of state
Gas dehydration with glycols	Flexible and predictive equations of state
Acid gas absorption with Methanol (rectisol) NMP (purisol)	Flexible and predictive equations of state

Application	Recommended Property Method
Acid gas absorption with Water Ammonia Amines Amines + methanol (amisol) Caustic Lime Hot carbonate	Electrolyte activity coefficients
Claus process	Flexible and predictive equations of state

Petrochemicals

Application	Recommended Property Method
Ethylene plant Primary fractionator	Petroleum fugacity correlations (and assay data analysis)
Light hydrocarbons separation train	Equations of state for high pressure hydrocarbon applications
Quench tower	Equations of state for high pressure hydrocarbon applications
Aromatics BTX extraction	Liquid activity coefficients (very sensitive to parameters)
Substituted hydrocarbons VCM plant Acrylonitrile plant	Equations of state for high pressure hydrocarbon applications
Ether production MTBE, ETBE, TAME	Liquid activity coefficients
Ethylbenzene and styrene plants	Equations of state for high pressure hydrocarbon applications and Ideal (with Watsol) or liquid activity coefficient
Terephthalic acid	Liquid activity coefficients(with dimerization in acetic acid section)

Chemicals

Application	Recommended Property Method
Azeotropic separations Alcohol separation	Liquid activity coefficients

Application	Recommended Property Method
Carboxylic acids Acetic acid plant	Liquid activity coefficients
Phenol plant	Liquid activity coefficients
Liquid phase reactions Estrification	Liquid activity coefficients
Ammonia plant	Equations of state for high pressure hydrocarbon applications (with k_{ij})
Fluorochemicals	Liquid activity coefficients (and HF equation of state)
Inorganic Chemicals Caustic Acids Phosphoric acid Sulphuric acid Nitric acid Hydrochloric acid	Electrolyte activity coefficients
Hydrofluoric acid	Electrolyte activity coefficient (and HF equation of state)

Coal Processing

Application	Recommended Property Method
Size reduction crushing, grinding	Solids processing (with coal analysis and particle size distribution)
Separation and cleaning sieving, cyclones, preciptition, washing	Solids processing (with coal analysis and and particle size distribution)
Combustion	Equations of state for high pressure hydrocarbon applications (with combustion databank)
Acid gas absorption	See Gas Processing earlier in this discussion.
Coal gasification and liquefaction	See Synthetic Fuel later in this discussion.

Power Generation

Application	Recommended Property Method
Combustion Coal Oil	Equations of state for high pressure hydrocarbon applications (with combustion databank) (and assay analysis with coal correlations) (and assay analysis)
Steam cycles Compressors Turbines	Steam tables
Acid gas absorption	See Gas Processing earlier in this discussion.

Synthetic Fuel

Application	Recommended Property Method
Synthesis gas	Equations of state for high pressure hydrocarbon applications
Coal gasification	Equations of state for high pressure hydrocarbon applications
Coal liquefaction	Equations of state for high pressure hydrocarbon applications with k_{ij} and assay analysis with coal correlations)

Environmental

Application	Recommended Property Method
Solvent recovery	Liquid activity coefficients
(Substituted) hydrocarbon stripping	Liquid activity coefficients
Acid gas stripping from Methanol (rectisol) NMP (purisol)	Flexible and predictive equations of state

Application	Recommended Property Method
Acid gas stripping from Water Ammonia Amines Amines + methanol (amisol) Caustic Lime Hot carbonate	Electrolyte activity coefficients
Claus process	Flexible and predictive equations of state
Acids Stripping Neutralization	Electrolyte activity coefficients

Water and Steam

Application	Recommended Property Method
Steam systems	Steam tables
Coolant	Steam tables

Mineral and Metallurgical Processes

Application	Recommended Property Method
Mechanical processing crushing, grinding, sieving, washing	Solids Processing (with inorganic databank)
Hydrometallurgy Mineral leaching	Electrolyte activity coefficients
Pyrometallurgy Smelter Converter	Solids Processing (with inorganic databank)

IDEAL Property Method

The IDEAL property method accommodates both Raoult's law and Henry's law. This method uses the:

- Ideal activity coefficient model for the liquid phase ($\gamma = 1$)
- Ideal gas equation of state $Pv = RT$ for the vapor phase
- Rackett model for liquid molar volume

The IDEAL property method is recommended for systems in which ideal behavior can be assumed, such as:

- Systems at vacuum pressures
- Isomeric systems at low pressures

In the vapor phase, small deviations from the ideal gas law are allowed. These deviations occur at:

- Low pressures (either below atmospheric pressure, or at pressures not exceeding 2 bar)
- Very high temperatures

Ideal behavior in the liquid phase is exhibited by molecules with either:

- Very small interactions (for example, paraffin of similar carbon number)
- Interactions that cancel each other out (for example, water and acetone)

The IDEAL property method:

- Can be used for systems with and without noncondensable components. Permanent gases can be dissolved in the liquid. You can use Henry's law, which is valid at low concentrations, to model this behavior.
- Does not include the Poynting correction
- Returns heat of mixing of zero
- Is used to initialize FLASH algorithm

The transport property models for the vapor phase are all well suited for ideal gases. The transport property models for the liquid phase are empirical equations for fitting experimental data.

The IDEAL property method is sometimes used for solids processing where VLE is unimportant (for example, in coal processing). For these, however, the SOLIDS property method is recommended. See Solids Handling Property Method for documentation on solid phase properties.

Mixture Types

Ideal mixtures with and without noncondensable components. You should not use IDEAL for nonideal mixtures.

Range

IDEAL is appropriate only at low pressure and low liquid mole fractions of the noncondensable components (if present).

Use of Henry's Law

To use Henry's law for noncondensable components, you must designate these components as Henry's components on the Components Henry-Comps form. Henry's constant model parameters (HENRY) must be available for the solute with at least one solvent. Use the **Methods | Parameters | Binary Interaction** form (**HENRY-1**) tab to enter Henry's constants or to review built-in parameters. Aspen Physical Property System contains an extensive collection of Henry's constants for many solutes in solvents. Solvents are water and other organic components. Aspen Physical Property System uses these parameters automatically when you specify the IDEAL property method.

The following table lists thermodynamic and transport property models used in IDEAL, and their minimum parameter requirements.

Parameters Required for the IDEAL Property Method

General

Property/Purpose	Parameter Requirements
Mass balance,	
Conversion Mass-basis↔ Mole-basis	MW
Conversion Stdvol-basis↔ Mole-basis	VLSTD
Using Free-water option: solubility of water in organic phase	WATSOL
Enthalpy of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Thermodynamic Properties

Properties	Models	Parameter Requirements
Vapor mixture fugacity coefficient	Ideal gas law	
Enthalpy, entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
Density	Ideal gas law	

Properties	Models	Parameter Requirements
Liquid mixture Fugacity coefficient	Ideal liquid activity coefficient	
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Solute: (VC or VLBROC)
Enthalpy, entropy	General Pure Component Heat of Vaporization	TC, (DHVLWT or DHVLDP)
Density	Rackett	TC, PC, (VC or VCRKT), (ZC or RKTZRA)

Transport Properties

Properties	Models	Parameter Requirements
Vapor mixture Viscosity	General Pure Component Vapor Viscosity	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal conductivity	General Pure Component Vapor Thermal Conductivity	MW or KVDIP
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	General Pure Component Liquid Surface Tension	(TC, PC, OMEGA) or SIGDIP
Liquid mixture Viscosity	General Pure Component Liquid Viscosity	MULAND or MULDIP
Thermal Conductivity	General Pure Component Liquid Thermal Conductivity	(MW, TC, TB) or KLDIP
Diffusivity	Wilke-Chang	MW, VB

Reference Correlations for Specific Components

These methods implement correlations designed to model specific sets of components very precisely. They should only be used to model the components they are based on.

Property Methods for Specific Components

Property Method	Model	Components
REFPROP	NIST Reference Fluid Thermodynamic and Transport Database	Water, natural gas, common hydrocarbons, and refrigerants
GERG2008	ISO-20765 (2008 extension of GERG-2004 equation of state)	Natural gas

REFPROP (NIST Reference Fluid Thermodynamic and Transport Properties Database)

Overview

REFPROP is an acronym for REFerence fluid PROPerties. This model, developed by the National Institute of Standards and Technology (NIST), provides thermodynamic and transport properties of industrially important fluids and their mixtures with an emphasis on refrigerants and hydrocarbons, especially natural gas systems.

REFPROP is based on the most accurate pure fluid and mixture models currently available. It implements three models for the thermodynamic properties of pure fluids: equations of state explicit in Helmholtz energy, the modified Benedict-Webb-Rubin equation of state, and an extended corresponding states (ECS) model. Mixture calculations employ a model that applies mixing rules to the Helmholtz energy of the mixture components; it uses a departure function to account for the departure from ideal mixing. Viscosity and thermal conductivity are modeled with either fluid-specific correlations, an ECS method, or in some cases the friction theory method.

REFPROP in the Aspen Physical Property System is provided under an agreement with the National Institute of Standards and Technology's (NIST) Standard Reference Data Program (SRDP).

For information about the version of REFPROP in use, see NIST-TRC Databank.

Fluids, models, and available properties

REFPROP in the Aspen Physical Property System includes 145 pure fluids:

- The typical natural gas constituents methane, ethane, propane, butane, 2,2-dimethylbutane, 2,3-dimethylbutane, isobutane, pentane, isopentane, 3-methylpentane, hexane, isohexane, heptane, octane, isooctane, nonane, decane, undecane, dodecane, carbon dioxide, carbon monoxide, hydrogen, nitrogen, and water

- The hydrocarbons acetone, acetylene, benzene, ethylbenzene, 1,3-butadiene, butene, cis-butene, cyclobutene, 1-butyne, cyclohexane, cyclopropane, n-docosane, ethylene, n-hexadecane, isobutene, neopentane, 1-pentene, propyne, trans-butene, toluene, methylcyclohexane, propadiene, n-propylcyclohexane, cyclopentane, m-xylene, o-xylene, p-xylene
- The HFCs R23, R32, R41, R125, R134a, R143a, R152a, R161, R227ea, R236ea, R236fa, R245ca, R245fa, R365mfc, R1234yf, R1234ze, R-E143a, R-E245cb2, R-E245fa2, R-E347mcc
- The HCFCs R21, R22, R123, R124, R141b, and R142b
- The traditional CFCs R11, R12, R13, R113, R114, and R115
- The fluorocarbons R14, R116, R218, C4F10, C5F12, C6F14, RC318, Novec649, R-1216, R1123, R1234zez, R1243zf, and R1336mzz
- The HCCs R-40 (methyl chloride), R-150 (1,2-dichloroethane), vinyl chloride, and chlorobenzene
- The "natural" refrigerants ammonia, carbon dioxide, propane, isobutane, and propylene
- The main air constituents nitrogen, oxygen, and argon
- The noble elements helium, argon, neon, krypton, and xenon
- The cryogens argon, carbon monoxide, deuterium, krypton, neon, nitrogen trifluoride, nitrogen, fluorine, chlorine, helium, methane, oxygen, normal hydrogen, parahydrogen, and orthohydrogen
- The fatty acid methyl esters (FAMEs) methyl linoleate, methyl linolenate, methyl oleate, methyl palmitate, and methyl stearate
- The siloxanes hexamethyldisiloxane, octamethylcyclotetrasiloxane, octamethyltrisiloxane, decamethylcyclopentasiloxane, decamethyltetrasiloxane, dodecamethylcyclehexasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane
- Water (as a pure fluid)
- Miscellaneous substances including carbonyl sulfide, dimethyl ether, diethyl ether, ethanol, heavy water, hydrogen sulfide, hydrogen chloride, methanol, nitrous oxide, sulfur hexafluoride, sulfur dioxide, trifluoroiodomethane, dimethyl carbonate, ethylene oxide, propylene oxide, monoethanolamine, diethanolamine, and ethylene glycol.

The REFPROP model uses the most accurate equations of state and models currently available:

- High accuracy Helmholtz energy equations of state, including international standard equations for water[1], R134a[2], R32[3], and R143a [4] and equations from the literature for ethane[5], propane[6], R125 [7], ammonia[8], carbon dioxide[9], and others
- High accuracy MBWR equations of state, including the international standard EOS for R123[10]
- The Bender equation of state for several of the "older" refrigerants,

including R14[11], R114[11], and RC318[11]

- An extended corresponding states model for fluids with limited data
- An excess Helmholtz energy model for mixture properties
- Experimentally based values of the mixture parameters are available for hundreds of mixtures
- Viscosity and thermal conductivity are based on fluid-specific correlations (where available), a modification of the extended corresponding states model, or the friction theory model

Available properties:

- Thermodynamic properties: Density (molar volume), fugacity, Enthalpy, Entropy, Gibbs free energy
- Transport properties: Thermal conductivity, Viscosity, Surface Tension

Important: For components that are not included in the valid REFPROP component list, the Aspen Physical Property System will ignore these components and calculate the physical properties for the remaining components that are on the list. Pure component properties of the non-REFPROP components will be missing. For mixture properties, the mole fractions used in the calculations will be re-normalized.

Cautions

The AGA8 equation of state model is not available in the REFPROP model in the Aspen Physical Property System. The GERG-2004 model, with its 2008 extensions, is available as the separate GERG2008 property method.

Enthalpy, entropy and Gibbs free energy values obtained from Aspen Plus using the REFPROP model are different from those calculated using the standalone REFPROP program distributed by NIST. This is because of the difference in the reference states used in the two programs. In Aspen Plus, the reference state is ideal gas at 298.15 K and 1 atm, while in the standalone REFPROP program [12], [13], the reference states are set up differently. Please see the information on reference state given below. However, the calculation of the departure function of these properties is the same.

The REFPROP model is designed to provide the most accurate thermophysical properties currently available for pure fluids and their mixtures. The present version is limited to vapor-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE), and vapor-liquid-liquid equilibrium (VLLE). The model does not know the location of the freezing line for mixtures. Certain mixtures can potentially enter into these areas without giving warnings to the user.

Some mixtures have components with a wide range of volatilities, as indicated by a critical temperature ratio greater than 2. Certain calculations, especially saturation calculations, may fail without generating warnings.

Two equations of state are available for hydrogen to account for the different quantum states of the molecule. These are implemented as two different components:

- Normal hydrogen should be used in applications where it was created and stored at 250 K or above, or when it was cooled to below 250 K and stored without a catalyst for less than a day.
- Para hydrogen should be used where hydrogen was catalyzed or stored for several days at the normal boiling point (NBP) and used at any temperature within 1 day of storage at the NBP.

Since the rate of conversion between quantum states is dependent on temperature, pressure, and the storage container, these values are only estimates. For more information, see the Jacobsen et al. [14] literature reference for hydrogen. Orthohydrogen is also available as a component for use in modeling hydrogen as a mixture of the two different quantum states.

Viscosity and thermal conductivity models are not available for some fluids. Therefore, REFPROP will not be able to return meaningful values for pure or mixture properties of systems that contain one or more of these fluids. These fluids are: SO2 (sulfur dioxide), SF6 (sulfur hexafluoride), Propyne, NF3 (nitrogen trifluoride), Fluorine, Deuterium, cyclopropane, carbonyl sulfide, C5F12 (dodecafluoropentane), C4F10 (decafluorobutane), benzene, toluene, acetone, R21 (dichlorofluoromethane), R236ea (1,1,1,2,3,3-hexafluoropropane), and R1336mzz (C4H2F6).

The lower temperature limit for pure Helium is 2.1768 K. Below this temperature, Helium is a super-fluid; its properties change dramatically and cannot be adequately represented by the current model.

Reference state

The absolute values of enthalpy, entropy, and Gibbs free energy at a single state point are meaningless. It is only the difference between two different state points that matter. Thus, the value for a single state point can be set to any arbitrary value. Many handbooks set the arbitrary state point so that the values of these properties are positive for most liquid or gas states.

In the Aspen Physical Property System, the reference state on which the values of the enthalpy and Gibbs free energy are based is:

- Setting enthalpy to the ideal gas enthalpy of formation of the component at 298.15 K and 1 atm (101325 Pa).
- Setting Gibbs free energy to the ideal gas Gibbs free energy of formation of the component at 298.15 K and 1 atm (101325 Pa).

In the REFPROP standalone program, there are three choices for the reference state on which the values of enthalpy and entropy are based:

- Setting enthalpy and entropy to zero for the saturated liquid at the normal boiling point (designated as NBP).
- Setting enthalpy and entropy to zero for the saturated liquid at -40 °C (designated as ASHRAE).

- Setting enthalpy to 200 kJ/kg and entropy to 1.0 kJ/(kg-K) for the saturated liquid at 0 °C (designated as IIR).

For detailed information on the reference states in Aspen Plus and REFPROP standalone program, please see help topics for the respective software.

Miscellaneous components in REFPROP and the valid temperature and pressure ranges

Component name	CAS number	Full Chemical Name	EOS Temperature and Pressure Limits
ACETONE	67-64-1	propanone	178.5-550 K, 700 Mpa
AMMONIA	7664-41-7	ammonia	195.495-700 K, 1000 MPa
ARGON	7440-37-1	argon	83.8058-2000 K,1000 MPa
CARBON-DIOXIDE	124-38-9	carbon dioxide	216.592-2000 K, 800 MPa
CARBON-MONOXIDE	630-08-0	carbon monoxide	68.16-500 K, 100 MPa
CARBONYL-SULFIDE	463-58-1	carbon oxide sulfide	134.3-650 K, 50 MPa
CHLORINE	7782-50-5	chlorine	172.17-440 K, 20 MPa
CHLOROBENZENE	108-90-7	chlorobenzene	227.9-700 K, 100 MPa
DEUTERIUM	7782-39-0	deuterium	18.71-423 K, 320 MPa
DIETHANOLAMINE	111-42-2	diethanolamine (DEA)	301.1-740 K, 5 MPa
DIETHYL-ETHER	60-29-7	diethyl ether	270-500 K, 40 MPa
DIMETHYL-CARBONATE	616-38-6	dimethyl ester carbonic acid	277.06-400 K, 60 MPa
DIMETHYL-ETHER	115-10-6	dimethyl ether	131.65-525 K, 40 MPa
ETHANOL	64-17-5	ethyl alcohol	250-650 K, 280 MPa
ETHYLENE-GLYCOL	107-21-1	ethylene glycol	260.6-750 K, 100 MPa
ETHYLENE-OXIDE	75-21-8	ethylene oxide	160.654-500 K, 10 MPa
FLUORINE	7782-41-4	fluorine	53.4811-300 K, 20 MPa
DEUTERIUM-OXIDE	7789-20-0	deuterium oxide	276.97-800 K, 100 MPa
HELIUM-4	7440-59-7	helium-4	2.1768**-1500 K, 100 MPa
HYDROGEN	1333-74-0	hydrogen (normal)	13.957-1000 K, 2000 MPa

Component name	CAS number	Full Chemical Name	EOS Temperature and Pressure Limits
HYDROGEN-PARA		parahydrogen	13.803-1000 K, 2000 MPa
HYDROGEN,-DIATOMIC,-ORTHO	999989-91-2	orthohydrogen	14.008-1000 K, 2000 MPa
HYDROGEN-CHLORIDE	7647-01-0	hydrogen chloride	155-330 K, 20 MPa
HYDROGEN-SULFIDE	7783-06-4	hydrogen sulfide	187.7-760 K, 170 MPa
KRYPTON	7439-90-9	krypton	115.775-750 K, 200 MPa
METHANOL	67-56-1	methanol	175.61-620 K, 800 MPa
MONOETHANOLAMINE	141-43-5	monoethanolamine (MEA)	283.7-675 K, 9 MPa
NEON	7440-01-9	neon	24.556-700 K, 700 MPa
NITROGEN	7727-37-9	nitrogen	63.151-2000 K, 2200 MPa
NITROGEN-TRIFLUORIDE	7783-54-2	nitrogen trifluoride	85-500 K, 50 MPa
NITROUS-OXIDE	10024-97-2	dinitrogen monoxide	182.33-525 K, 50 MPa
OXYGEN	7782-44-7	oxygen	54.361-2000 K, 82 MPa
DECAFLUOROBUTANE	355-25-9	decafluorobutane	189-500 K, 30 MPa
PERFLUORO-N-HEXANE	355-42-0	tetradecafluorohexane	187.07-450 K, 40 MPa
PERFLUORO-N-PENTANE	678-26-2	dodecafluoropentane	200-500 K, 30 MPa
PROPYLENE-OXIDE	75-56-9	propylene oxide	161.244-489 K, 10 MPa
SULFUR-DIOXIDE	7446-09-5	sulfur dioxide	197.7-525 K, 35 MPa
SULFUR-HEXAFLUORIDE	2551-62-4	sulfur hexafluoride	223.555-625 K, 150 MPa
TRIFLUOROIODOMETHANE	2314-97-8	trifluoroiodomethane	120-420 K, 20 MPa
VINYL-CHLORIDE	75-01-4	vinyl chloride	190-450 K, 10 MPa
WATER	7732-18-5	water	273.16-2000 K, 1000 MPa
XENON	7440-63-3	xenon	161.405-750 K, 700 MPa

Hydrocarbons

Component name	CAS number	Full Chemical Name	EOS Temperature and Pressure Limits
ACETYLENE	74-86-2	acetylene	191.75-310 K, 10 MPa

Component name	**CAS number**	**Full Chemical Name**	**EOS Temperature and Pressure Limits**
BENZENE	71-43-2	benzene	278.7-635 K, 78 MPa
N-BUTANE	106-97-8	n-butane	134.895-575 K, 69 MPa
1,3-BUTADIENE	106-99-0	1,3-butadiene	164.25-426 K, 10 MPa
1-BUTENE	106-98-9	1-butene	87.8-525 K, 70 MPa
1-BUTYNE	107-00-6	1-butyne	147.44-432 K, 10 MPa
CIS-2-BUTENE	590-18-1	cis-2-butene	134.3-525 K, 50 MPa
CYCLOBUTENE	822-35-5	cyclobutene	150-448 K, 10 MPa
CYCLOHEXANE	110-82-7	cyclohexane	279.47-700 K, 80 MPa
CYCLOPENTANE	287-92-3	cyclopentane	179.72-600 K, 200 MPa
CYCLOPROPANE	75-19-4	cyclopropane	273-473 K, 28 MPa
N-DECANE	124-18-5	decane	243.5-675 K, 800 MPa
N-DOCOSANE	629-97-0	docosane	317.04-1000 K, 50 MPa
N-DODECANE	112-40-3	dodecane	263.6-700 K, 700 MPa
ETHANE	74-84-0	ethane	90.368-675 K, 900 MPa
ETHYLBENZENE	100-41-4	phenylethane	178.2-700 K, 60 MPa
ETHYLENE	74-85-1	ethene	103.986-450 K, 300 MPa
N-HEPTANE	142-82-5	heptane	182.55-600 K, 100 MPa
N-HEXADECANE	544-76-3	hexadecane	291.329-800 K, 50 MPa
N-HEXANE	110-54-3	hexane	177.83-600 K, 100 MPa
ISOBUTANE	75-28-5	2-methylpropane	113.73-575 K, 35 MPa
ISOBUTYLENE	115-11-7	2-methyl-1-propene	132.4-550 K, 50 MPa
2,2,4-TRIMETHYLPENTANE	540-84-1	isooctane	165.77-600 K, 1000 MPa
2-METHYL-PENTANE	107-83-5	2-methylpentane	119.6-550 K, 1000 MPa
2-METHYL-BUTANE	78-78-4	2-methylbutane	112.65-500 K, 1000 MPa
METHANE	74-82-8	methane	90.6941-625 K, 1000 MPa
METHYLCYCLOHEXANE	108-87-2	methylcyclohexane	146.7-600 K, 500 MPa
3-METHYL-PENTANE	96-14-0	3-methylpentane	110.263-550 K, 1000 MPa
2,2-DIMETHYL-BUTANE	75-83-2	2,2-dimethylbutane	174.2-575 K, 1000 MPa

Component name	CAS number	Full Chemical Name	EOS Temperature and Pressure Limits
2,3-DIMETHYL-BUTANE	79-29-8	2,3-dimethylbutane	145.05-550 K, 1000 MPa
2,2-DIMETHYL-PROPANE	463-82-1	2,2-dimethylpropane	256.6-550 K, 200 MPa
N-NONANE	111-84-2	nonane	219.7-600 K, 800 MPa
N-OCTANE	111-65-9	octane	216.37-600 K, 100 MPa
N-PENTANE	109-66-0	pentane	143.47-600 K, 100 MPa
1-PENTENE	109-67-1	1-pentene	107.797-466 K, 10 MPa
PROPADIENE	463-49-0	propadiene	136.65-400 K, 10 MPa
PROPANE	74-98-6	propane	85.53-625 K, 1000 MPa
N-PROPYLCYCLOHEXANE	1678-92-8	n-propylcyclohexane	178.2-650 K, 50 MPa
PROPYLENE	115-07-1	propene	87.953-575 K, 1000 MPa
METHYL-ACETYLENE	74-99-7	propyne	273-474 K, 32 MPa
TOLUENE	108-88-3	methylbenzene	178-700 K, 500 MPa
TRANS-2-BUTENE	624-64-6	trans-2-butene	167.6-525 K, 50 MPa
N-UNDECANE	1120-21-4	undecane	247.541-700 K, 500 MPa
M-XYLENE	108-38-3	1,3-methylbenzene	225.3-700 K, 200 MPa
O-XYLENE	95-47-6	1,2-methylbenzene	247.985-700 K, 70 MPa
P-XYLENE	106-42-3	1,4-methylbenzene	286.4-700 K, 200 MPa

Fatty Acid Methyl Esters

Component name	CAS number	Full Chemical Name	EOS Temperature and Pressure Limits
METHYL-LINOLEATE	112-63-0	methyl (Z,Z)-9,12-octadecadienoate	238.1-1000 K, 50 MPa
METHYL-LINOLENATE	301-00-8	methyl (Z,Z,Z)-9,12,15-octadecatrienoate	218.65-1000 K, 50 MPa
METHYL-OLEATE	112-62-9	methyl cis-9-octadecenoate	253.47-1000 K, 50 MPa
METHYL-PALMITATE	112-39-0	methyl hexadecanoate	242-1000 K, 50 MPa
METHYL-STEARATE	112-61-8	methyl octadecanoate	311.4- 1000 K, 50 MPa

Siloxanes

Component name	CAS number	EOS Temperature and Pressure Limits
HEXAMETHYLDISILOXANE	107-46-0	273-673 K, 30 MPa
OCTAMETHYLCYCLOTETRASILOXANE	556-67-2	300-673 K, 30 MPa
OCTAMETHYLTRISILOXANE	107-51-7	187.2-673 K, 30 MPa
DECAMETHYLCYCLOPENTASILOXANE	541-02-6	300-673 K, 30 MPa
DECAMETHYLTETRASILOXANE	141-62-8	205.2-673 K, 30 MPa
DODECAMETHYLCYCLOHEXASILOXANE	540-97-6	270.2-673 K, 30 MPa
DODECAMETHYLPENTASILOXANE	141-63-9	192-673 K, 30 MPa
TETRADECAMETHYLHEXASILOXANE	107-52-8	300-673 K, 30 MPa

Refrigerants

Component name	CAS number	Refrigerant name	EOS Temperature and Pressure Limits
DODECAFLUORO-2-METHYLPENTAN-3-ONE	756-13-8	Novec649	165-500 K, 50 MPa
TRICHLOROFLUOROMETHANE	75-69-4	R11	162.68-625 K, 30 MPa
DICHLORODIFLUOROMETHANE	75-71-8	R12	116.099-525 K, 200 MPa
CHLOROTRIFLUOROMETHANE	75-72-9	R13	92-403 K, 35 MPa
CARBON-TETRAFLUORIDE	75-73-0	R14	120-623 K, 51 MPa
DICHLOROMONOFLUOROMETHANE	75-43-4	R21	200-473 K, 138 MPa
CHLORODIFLUOROMETHANE	75-45-6	R22	115.73-550 K, 60 MPa
TRIFLUOROMETHANE	75-46-7	R23	118.02-475 K, 120 MPa
DIFLUOROMETHANE	75-10-5	R32	136.34-435 K, 70 MPa
METHYL-CHLORIDE	74-87-3	R40	230-630 K, 100 MPa
METHYL-FLUORIDE	593-53-3	R41	129.82-425 K, 70 MPa
1,2,2-TRICHLORO-1,1,2-TRIFLUOROE	76-13-1	R113	236.93-525 K, 200 MPa
1,2-DICHLORO-1,1,2,2-TETRAFLUORO	76-14-2	R114	273.15-507 K, 21 MPa
CHLOROPENTAFLUOROETHANE	76-15-3	R115	173.75-550 K, 60 MPa

Component name	CAS number	Refrigerant name	EOS Temperature and Pressure Limits
PERFLUOROETHANE	76-16-4	R116	173.1-425 K, 50 MPa
1,1-DICHLORO-2,2,2-TRIFLUOROETHA	306-83-2	R123	166-600 K, 40 MPa
HFO-1234YF	754-12-1	R1234yf	220-410 K, 30 MPa
TRANS-1,3,3,3-TETRAFLUORPROPENE	29118-24-9	R1234ze	168.62-420 K, 20 MPa
2-CHLORO-1,1,1,2-TETRAFLUOROETHA	2837-89-0	R124	120-470 K, 40 MPa
PENTAFLUOROETHANE	354-33-6	R125	172.52-500 K, 60 MPa
1,1,1,2-TETRAFLUOROETHANE	811-97-2	R134a	169.85-455 K, 70 MPa
1,1-DICHLORO-1-FLUOROETHANE	1717-00-6	R141b	169.68-500 K, 400 MPa
1-CHLORO-1,1-DIFLUOROETHANE	75-68-3	R142b	142.72-470 K, 60 MPa
1,1,1-TRIFLUOROETHANE	420-46-2	R143a	161.34-650 K, 100 MPa
1,2-DICHLOROETHANE	107-06-2	R150	237.52-600 K, 50 MPa
1,1-DIFLUOROETHANE	75-37-6	R152a	154.56-500 K, 60 MPa
ETHYL-FLUORIDE	353-36-6	R161	130-400 K, 50 MPa
OCTAFLUOROPROPANE	76-19-7	R218	125.45-440 K, 20 MPa
1,1,1,2,3,3,3-HEPTAFLUOROPROPANE	431-89-0	R227ea	146.35-475 K, 60 MPa
1,1,1,2,3,3-HEXAFLUOROPROPANE	431-63-0	R236ea	242-500 K, 60 MPa
*HFC-236FA	690-39-1	R236fa	179.52-500 K, 40 MPa
1,1,2,2,3-PENTAFLUOROPROPANE	679-86-7	R245ca	200-500 K, 60 MPa
1,1,1,3,3-PENTAFLUOROPROPANE	460-73-1	R245fa	171.05-440 K, 200 MPa
1,1,1,3,3-PENTAFLUOROBUTANE	406-58-6	R365mfc	239-500 K, 35 MPa
*TRIFLUOROETHYLENE	359-11-5	R1123	200-480 K, 20 MPa
HEXAFLUOROPROPYLENE	116-15-4	R1216	117.654-400 K, 12 MPa
*C3H2F4-N2	29118-25-0	R1234zez	238-440 K, 34 MPa
3,3,3-TRIFLUOROPROPENE	677-21-4	R1243zf	200-430 K, 40 MPa
*C4H2F6	692-49-9	R1336mzz	182.65-500 K, 40 MPa
OCTAFLUOROCYCLOBUTANE	115-25-3	RC318	233.35-623 K, 60 MPa
*METHYL-TRIFLUOROMETHYL-ETHER	421-14-7	RE143a	240-420 K, 7.2 MPa

Component name	CAS number	Refrigerant name	EOS Temperature and Pressure Limits
PENTAFLUOROETHYL-METHYL-ETHER	22410-44-2	RE245cb2	250-500 K, 20 MPa
2-DIFLUOROMETHOXY-1,1,1-TRIFLURO	1885-48-9	RE245fa2	250-500 K, 400 MPa
HEPTAFLUOROPROPYL-METHYL-ETHER	375-03-1	RE347mcc	250-500 K, 20 MPa

* Component only available in NIST database.

** Although the lower limit of applicability for the helium model is 2.1768 K, the global flash temperature lower limit is by default 10 K. To perform calculations with helium below 10 K, change the **Lower limit** for **Temperature** on the **Setup | Calculation Options | Flash Convergence** sheet. If using Aspen Properties within another program, this default needs to be set in Aspen Properties while configuring properties for that program.

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GERG2008 Property Method

The GERG2008 property method is based on the 2008 extension of the GERG-2004 equation of state model for calculations of thermodynamic properties and phase equilibrium of natural gases and other mixtures consisting of natural gas components.

This model was developed under the auspices of the Groupe Européen de Recherches Gazières (GERG) in cooperation with the German technical and Scientific Association on Gas and Water and European natural gas companies (E.ON Ruhrgas, Germany; Enagas, Spain; Gasunie, The Netherlands; Gaz de France, France; Snam Rete Gas, Italy; and Statoil, Norway).

This is a highly accurate, wide-range equation of state that has been adopted as a standard (ISO-20765) international reference equation suitable for all natural gas applications, including processing, transportation, and storage of natural gas. The model is applicable to 21 natural gas components and their mixtures, including Methane, Nitrogen, Carbon dioxide, Ethane, Propane, n-Butane, Isobutane, n-Pentane, Isopentane, n-Hexane, n-Heptane, n-Octane, n-Nonane, n-Decane, Hydrogen, Oxygen, Carbon monoxide, Water, Helium, Argon, and Hydrogen sulfide. Detailed information on each component is given in the table below.

List of the 21 main and secondary natural gas components and their equations of state[a]

Pure substance	Reference	Range of Valid Temperatures (K)	Maximum Valid Pressure (MPa)	Number of terms
Main Components				
Methane	Klimeck (2000)	90 – 623	300	24
Nitrogen	Klimeck (2000)	63 – 700	300	24
Carbon dioxide	Klimeck (2000)	216[b] – 900	300	22
Ethane	Klimeck (2000)	90 – 623	300	24
Secondary alkanes				
Propane	Span & Wagner (2003)	85 – 623	100	12
n-Butane	Span & Wagner (2003)	134 – 693	70	12
Isobutane	Span & Wagner (2003)	113 – 573	35	12
n-Pentane	Span & Wagner (2003)	143 – 573	70	12
Isopentane	Span (2000)	112–500	35	12
n-Hexane	Span & Wagner (2003)	177 – 548	100	12
n-Heptane	Span & Wagner (2003)	182 – 523	100	12
n-Octane	Span & Wagner (2003)	216 – 548	100	12
n-Nonane	Lemmon & Span (2006)	219 – 600	800	12
n-Decane	Lemmon & Span (2006)	243 – 675[e]	800	12
Other secondary components				
Hydrogen[c]	GERG (2007)	14 – 700	300	14
Oxygen	Span & Wagner (2003)	54 – 303	100	12

Pure substance	Reference	Range of Valid Temperatures (K)	Maximum Valid Pressure (MPa)	Number of terms
Carbon monoxide	GERG (2007)	68 – 400	100	12
Water	GERG (2007)	273 – 1273	100	16
Helium[d]	GERG (2007)	2.2 – 573	100	12
Argon	Span & Wagner (2003)	83 – 520	100	12
Hydrogen sulfide	Lemmon & Span (2006)	187 – 760	170	12

a The tabulated references correspond to the equations for the residual part of the Helmholtz free energy of the considered pure substances. The equations of Jaeschke and Schley (1995) for the isobaric heat capacity in the ideal-gas state were used to derive the Helmholtz free energy of the ideal gas for all components.

b The equation can be extrapolated from the triple point temperature down to 90 K (see Sec. 4.11.1).

c Represents equilibrium hydrogen.

d Represents helium-4. The lower temperature limit of the equation of state is the lambda point at which helium I transitions to helium II.

e The upper temperature limit has been set higher than the onset of decomposition of the fluid.

Applicability

The GERG2008 model can be applied to natural gases, rich natural gases (natural gases that contain large amounts of ethane and heavier alkanes), liquefied natural gases, liquefied petroleum gases, highly compressed natural gases and hydrogen-hydrocarbon mixtures, such as Hythane in the homogeneous gas, liquid, and supercritical regions as well as in the vapor-liquid equilibrium (VLE) region.

The equation of state is based on pure substance equations of state for each applicable component (as shown in the table above) and correlation equations for binary mixtures consisting of these components. This allows predictive description of multi-component mixtures over a wide range of compositions. The equation of state was developed and tested using an extensive database of binary mixtures, natural gases, and other multi-component mixtures data of over 100,000 data points for the thermal and caloric properties. The data used cover the homogeneous gas, liquid, and supercritical regions as well as vapor-liquid equilibrium (VLE) states. The types of data used include: PVT, isochoric heat capacity (Cv), speed of sound (w), isobaric heat capacity (Cp), enthalpy difference, excess molar enthalpy, saturated liquid density, and VLE data. About 75% of the data are for binary mixtures, while the remaining 25% are for multi-component mixtures. Almost 70% of the mixture data describe a PVT relation, more than 20% of the data are vapor-liquid equilibrium state points, and less than 10% account for caloric properties. About 50% of the available binary mixture data were used for model development while the remaining data were used for model validation.

The model cannot be used for components other than the ones listed above.

The GERG2008 model is available in Aspen Plus through the RefProp program developed by the National Institute of Standards and Technology (NIST).

Range of Validity and Estimates of Uncertainty

The GERG2008 model is valid in the homogeneous gas, liquid, and supercritical regions and in the vapor-liquid states. Due to the vast amount of experimental data for the different binary and multi-component mixtures, and the varying real mixture behavior, which strongly depends on temperature, pressure and composition, it is impossible to discuss each binary and multi-component system separately. In general, there are no restrictions concerning the composition range, but the uncertainty is mostly unknown for the composition ranges not covered by the experimental data.

The range of validity of the model related to the calculation of thermal and caloric properties of mixtures is divided into three parts: the normal range and the extended range.

In the normal range, the validity covers temperatures of 90 K ≤ T ≤ 450 K and pressures of p ≤ 35 MPa. This range corresponds to the use of the equation in applications using natural gas and related mixtures in pipeline transport, natural gas storage, and improved processes with liquefied natural gas.

The uncertainty for the important properties and phases are as follow:

- The uncertainty in gas phase density is < 0.1% for the temperature range from 250 – 450 K and pressure up to 35 MPa for various types of natural gases, including natural gases rich in nitrogen, rich in carbon dioxide, rich in ethane, rich in hydrogen, and natural gases containing considerable amounts of propane, and heavier alkanes, carbon monoxide, or oxygen and other mixtures consisting of the 21 natural gas components. The great majority of experimental densities for various rich natural gases containing large amounts of carbon dioxide (up to 20%), ethane (up to 18%), propane (up to 14%), n-butane (up to 6%), n-pentane (up to 0.5%), and n-hexane (0.2%) are reproduced to within ± (0.1 – 0.3)% over the temperature range 280 K to 350 K and pressure up to 30 MPa.
- The uncertainty in gas phase speed of sound is < 0.1% in the temperature range from 270 K to 450 K and pressures up to 20 MPa, and in the temperature range from 250 K to 270 K at pressures up to 12 MPa.

At higher pressures, the uncertainty is < (0.2 – 0.3)%.

- The uncertainty in gas phase isobaric enthalpy difference is < (0.2 – 0.5)%.
- The uncertainty for isobaric and isochoric heat capacity (Cp and Cv, respectively) in the homogeneous gas, liquid, and supercritical regions is ±(1 – 2)%
- The uncertainty for liquid phase isobaric enthalpy difference is ± (0.5 – 1)%.
- The uncertainty in liquid phase density is ⌖(0.1 – 0.5)%.for pressures up to 40 MPa for many binary and multi-component mixtures, including LNG-like mixtures and mixtures of light and heavy hydrocarbons.
- The uncertainty for saturated liquid density for the same types of mixtures in the temperate range from 100 K to 140 K, which is very important for processes with liquefied natural gas, is < (0.1 – 0.3)%.
- Vapor-liquid equilibrium data of binary and multi-component mixtures as well as dew points of natural gases and hydrocarbon mixtures are accurately described. The most accurate vapor pressure data for binary and ternary mixtures consisting of the natural gas main components (methane, nitrogen, carbon dioxide, and ethane), as well as propane, n-butane and isobutene are reproduced to within their experimental uncertainty (~ (1-3)%). Certain other mixtures have higher uncertainty of up to 5% or more. Accurate experimental vapor phase compositions are described to within ±(0.5 – 1) mole %.

The extended range of validity covers temperatures of 60 K ≤ T ≤ 700 K and pressures of p ≤ 70 MPa and has the following uncertainty:

- The uncertainty of gas phase density is (0.2 – 0.5)% at temperatures and pressures outside the normal range of validity
- Density data of certain binary mixtures are described to within ±(0.5 – 1)% at pressures up to 100 MPa or more.
- The current data situation outside the normal range does not allow for well-founded estimates of uncertainty of other thermodynamic properties.

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Property Methods for Petroleum Mixtures

The property methods in the following table are designed for mixtures of hydrocarbons and light gases. K-value models and liquid fugacity correlations are used at low and medium pressures. Petroleum-tuned equations of state are used at high pressures. The hydrocarbons can be from natural gas or crude oil: that is, complex mixtures that are treated using pseudocomponents. These property methods are often used for refinery applications. Density and transport properties are calculated by API procedures when possible.

The following table lists the common and the distinctive models of the property methods. The parameter requirements of the distinctive models are given in the tables labeled:

- Parameters Required for the CHAO-SEA Property Method (see CHAO-SEA)
- Parameters Required for the GRAYSON Property Method (see GRAYSON)
- Parameters Required for the PENG-ROB (see PENG-ROB)
- Parameters Required for the RK-SOAVE Property Method (see RK-SOAVE)

Parameter requirements for the common models are in the table labeled Parameters Required for Common Models. For details on these models, see *Physical Property Models*.

Property Methods for Petroleum Mixtures

Liquid Fugacity and K-Value Models

Property Method Name	Models
BK10	Braun K10 K-value model

Property Method Name	Models
CHAO-SEA	Chao-Seader liquid fugacity, Scatchard-Hildebrand activity coefficient
GRAYSON/GRAYSON2	Grayson-Streed liquid fugacity, Scatchard-Hildebrand activity coefficient
MXBONNEL	Maxwell-Bonnell liquid fugacity

Petroleum-Tuned Equations of State

Property Method Name	Models
HYSPR	Aspen HYSYS Peng-Robinson
HYSSRK	Aspen HYSYS Soave-Redlich-Kwong
PENG-ROB	Peng-Robinson
RK-SOAVE	Redlich-Kwong-Soave
SRK	Soave-Redlich-Kwong
SRK-KD	SRK-Kabadi-Danner
SRK-ML	SRK-ML

Common Models for Property Methods for Petroleum Mixtures

Property	Model
Liquid enthalpy	Lee-Kesler
Liquid molar volume	API
Vapor viscosity	General Pure Component Vapor Viscosity
Vapor thermal conductivity	General Pure Component Vapor Thermal Conductivity
Vapor diffusivity	Dawson-Khoury-Kobayashi
Surface tension	API surface tension
Liquid viscosity	API
Liquid thermal conductivity	General Pure Component Liquid Thermal Conductivity
Liquid diffusivity	Wilke-Chang

Liquid Fugacity and K-Value Model Property Methods

The BK10 property method is generally used for vacuum and low pressure applications (up to several atm). The CHAO-SEA property method and the GRAYSON property method can be used at higher pressures. GRAYSON has the widest ranges of applicability (up to several tens of atm). For hydrogen-rich systems, GRAYSON is recommended.

These property methods are less suited for high-pressure applications in refinery (above about 50 atm). Petroleum-tuned equation of state property methods are preferred for high pressures.

These property methods are not suited for conditions close to criticality, as occur in light oil reservoirs, transportation of gas by pipelines, and in some gas processing applications. Standard equations of state for non-polar components are preferred. If polar compounds are present, such as in gas treatment, use flexible and predictive equations of state for polar compounds.

BK10

The BK10 property method uses the Braun K-10 K-value correlations. The correlations were developed from the K10 charts for both real components and oil fractions. The real components include 70 hydrocarbons and light gases. The oil fractions cover boiling ranges 450 – 700 K (350 – 800°F). Proprietary methods were developed to cover heavier oil fractions.

Mixture Types

Best results are obtained with purely aliphatic or purely aromatic mixtures with normal boiling points ranging from 450 to 700 K. For mixtures of aliphatic and aromatic components, or naphtenic mixtures, the accuracy decreases. For mixtures with light gases, and medium pressures, CHAO-SEA or GRAYSON are recommended.

Range

The BK10 property method is suited for vacuum and low pressure applications (up to several atm). For high pressures, petroleum-tuned equations of state are best suited.

The applicable temperature range of the K10 chart is 133 – 800 K (-220 – 980°F). It can be used up to 1100 K (1520°F).

The parameters for the Braun K-10 are all built-in. You do not need to supply them. See Parameters Required for Common Models for parameter requirements of models common to petroleum property methods.

CHAO-SEA

The CHAO-SEA property method uses the:

- Chao-Seader correlation for reference state fugacity coefficient
- Scatchard-Hildebrand model for activity coefficient
- Redlich-Kwong equation of state for vapor phase properties
- Lee-Kesler equation of state for liquid and vapor enthalpy
- API method for liquid molar volume, viscosity and surface tension
- Models listed in the tables labeled Parameters Required for the CHAO-SEA Property Method (see below), and Parameters Required for Common Models

The tables labeled Parameters Required for the CHAO-SEA Property Method and Parameters Required for Common Models provide thermodynamic and transport property models, and their parameter requirements.

The CHAO-SEA property method is predictive. It can be used for crude towers, vacuum towers, and some parts of the ethylene process. It is not recommended for systems containing hydrogen.

Mixture Types

The CHAO-SEA property method was developed for systems containing hydrocarbons and light gases, such as carbon dioxide and hydrogen sulfide, but with the exception of hydrogen. If the system contains hydrogen, use the GRAYSON property method.

Range

Use the CHAO-SEA property method for systems with temperature and pressure limits of:

$200 < T < 533$ K

$0.5 < T_{ri} < 1.3$

$T_{rm} < 0.93$

$P < 140$ atm

Where:

T_{ri} = Reduced temperature of a component

T_{rm} = Reduced temperature of the mixture

Do not use this property method at very high pressures, especially near the mixture critical point, because of anomalous behavior in these regions.

Parameters Required for the CHAO-SEA Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Redlich-Kwong	TC, PC
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Redlich-Kwong	TC, PC
Liquid mixture Fugacity coefficient, Gibbs free energy	Scatchard-Hildebrand activity coefficient	TC, DELTA, VLCVT1; GMSHVL
	Chao-Seader pure component fugacity coefficient	TC, PC, OMEGA

GRAYSON/ GRAYSON2

The GRAYSON property method uses the:

- Grayson-Streed correlation for reference state fugacity coefficients
- Scatchard-Hildebrand model for activity coefficients
- Redlich-Kwong equation of state for vapor phase properties
- Lee-Kesler equation of state for liquid and vapor enthalpy
- API method for liquid molar volume, viscosity and surface tension

The GRAYSON2 property method uses the:

- Grayson-Streed correlation with Chao-Seader acentric factors for liquid fugacities
- Scatchard-Hildebrand model for activity coefficients with special handling for water
- Redlich-Kwong equation of state for vapor phase fugacity coefficients
- Redlich-Kwong equation of state for liquid and vapor phase properties (enthalpies and volumes). Water enthalpy calculated from NBS steam tables
- TRAPP model for transport properties

The GRAYSON2 method is provided for compatibility with RT-Opt version 10 simulations. Users building new simulations should use GRAYSON.

Refer to the tables labeled Parameters Required for the GRAYSON Property Method (below) and Parameters Required for Common Models for thermodynamic and transport property models, and their parameter requirements.

The GRAYSON/GRAYSON2 property methods are predictive. They can be used for crude towers, vacuum towers, and some parts of the ethylene process. They are recommended for systems containing hydrogen.

Mixture Types

The GRAYSON/GRAYSON2 property methods were developed for systems containing hydrocarbons and light gases, such as carbon dioxide and hydrogen sulfide. They are recommended over the CHAO-SEA property method when the system contains hydrogen.

Range

The GRAYSON/GRAYSON2 property methods should give reasonable results for temperatures from 60° F to 800° F for pressures up to 3000 psia. They should be used with caution at pressures above 600 psia and temperatures below 60° F. These methods are not recommended for modeling separations of close-boiling components (e.g. isomers). Do not use these property methods at very high pressures, especially near the mixture critical point, because of anomalous behavior in these regions.

Parameters Required for the GRAYSON Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Redlich-Kwong	TC, PC
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Redlich-Kwong	TC, PC
Liquid mixture Fugacity coefficient, Gibbs free energy	Scatchard-Hildebrand activity coefficient	TC, DELTA, VLCVT1;GMSHVL
	Grayson-Streed pure component fugacity coefficient	TC, PC, OMEGA

HYSPR

The HYSPR property method implements the Peng-Robinson (PR) property package from Aspen HYSYS. This package is ideal for VLE calculations as well as calculating liquid densities for hydrocarbon systems. Several enhancements to the original PR model were made to extend its range of applicability and to improve its predictions for some non-ideal systems. However, in situations where highly non-ideal systems are encountered, the use of activity coefficient models is recommended.

The PR property package rigorously solves any single-, two-, or three-phase system with a high degree of efficiency and reliability and is applicable over a wide range of conditions:

- Temperature Range > -271°C or -456°F
- Pressure Range < 100,000 kPa or 15,000 psia

The PR property package also contains 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.

For Oil, Gas, or Petrochemical applications, the PR EOS is the generally recommended property package. The PR property package is generally used for the following simulations:

- TEG Dehydration
- TEG Dehydration with Aromatics
- Cryogenic Gas Processing
- Air Separation
- Atm Crude Towers
- Vacuum Towers
- High H2 Systems
- Reservoir Systems
- Hydrate Inhibition
- Crude Systems

Parameters used by the HYSPR property method include:

- HPRKIJ: HYSYS Peng-Robinson EOS binary parameter
- OMGHPR: OMEGA for HYSYS Peng-Robinson EOS
- PCHPR: Critical pressure
- TCHPR: Critical temperature
- VTHPR: Volume Translation Parameter

These parameters and others used by HYSPR are available in the HYSYS databank. When using HYSPR it is recommended to place the HYSYS databank in the search order before other databanks.

When HPRKIJ is missing, it is estimated from critical volume:

$$k_{ij} = \frac{1-(V_{c,i}V_{c,j})^{1/6}}{\frac{1}{2}\left(V_{c,i}^{1/3}+V_{c,j}^{1/3}\right)}$$

Aspen HYSYS uses the same estimate, but may obtain slightly different values because the databank in the Aspen Physical Property System stores values to a greater precision. Also, Aspen HYSYS reports all parameters, while the Aspen Physical Property System does not report estimated parameter values.

The liquid thermal conductivity model uses API methods rather than the HYSYS model for pseudocomponents:

- API equation 12A3.2-1 for normal boiling point T_b above 337 K
- API equation 12A1.2-1 for other components with molecular weight above 140 and reduced temperature $T_r=T/T_c$ below 0.8

With option code 1 set to 1 in KL2HPR and KL0HPR, API equation 12A1.2-1 is used for all components.

Option code 1 of ESHPR and ESHPR0 controls the volume root search method. The default is 0, to use an analytical solution. This analytical solution may produce a wrong root in some cases, such as with some pure water streams. If you get results showing the wrong phase with HYSPR and such streams, change this option code to 1 to use the numerical solution. See Option Codes for Equation of State Models in *Physical Property Models* for information about other option codes.

For more information on the PR package, see Aspen HYSYS help.

HYSSRK

The HYSSRK property method implements the Soave-Redlich-Kwong (SRK) property package from Aspen HYSYS. In many cases, this model provides comparable results to the Peng-Robinson (HYSPR method), but its range of application is significantly more limited:

- Temperature Range > -143 °C or -225 °F
- Pressure Range < 5,000 psia or 35,000 kPa

The SRK EOS should not be used for non-ideal chemicals such as alcohols, acids or other components. These chemicals are more accurately handled by activity coefficient models (highly non-ideal) or other equations of state (moderately non-ideal).

The SRK property package is generally used for the following simulations:

- TEG Dehydration
- Sour Water
- Cryogenic Gas Processing
- Air Separation
- Atm Crude Towers
- Vacuum Towers
- High H2 Systems
- Reservoir Systems
- Hydrate Inhibition
- Chemical systems
- HF Alkylation
- TEG Dehydration with Aromatics

The proprietary enhancements to the SRK property package allow the SRK equation of state (EOS) to correctly represent vacuum conditions and heavy components (a problem with traditional EOS methods), as well as handle the light ends and high-pressure systems.

The SRK property package contains 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.

Parameters used by the HYSSRK property method include:

- HSRKIJ: HYSYS Soave-Redlich-Kwong EOS binary parameter
- OMHSRK: OMEGA for HYSYS Soave-Redlich-Kwong EOS
- PCHSRK: Critical pressure
- TCHSRK: Critical temperature
- VTHSRK: Volume Translation Parameter

These parameters and others used by HYSSRK are available in the HYSYS databank. When using HYSSRK , it is recommended to place the HYSYS databank in the search order before other databanks.

When HSRKIJ is missing, it is estimated from critical volume:

$$k_{ij} = \frac{1-(V_{c,i}V_{c,j})^{1/6}}{\frac{1}{2}\left(V_{c,i}^{1/3}+V_{c,j}^{1/3}\right)}$$

Aspen HYSYS uses the same estimate, but may obtain slightly different values because the databank in the Aspen Physical Property System stores values to a greater precision. Also, Aspen HYSYS reports all parameters, while the Aspen Physical Property System does not report estimated parameter values.

The liquid thermal conductivity model uses API methods rather than the HYSYS model for pseudocomponents:

- API equation 12A3.2-1 for normal boiling point T_b above 337 K
- API equation 12A1.2-1 for other components with molecular weight above 140 and reduced temperature $T_r=T/T_c$ below 0.8

With option code 1 set to 1 in KL2HSRK and KL0HSRK, API equation 12A1.2-1 is used for all components.

Option code 1 of ESHSRK and ESHSRK0 controls the volume root search method. The default is 0, to use an analytical solution. This analytical solution may produce a wrong root in some cases, such as with some pure water streams. If you get results showing the wrong phase with HYSSRK and such streams, change this option code to 1 to use the numerical solution. See Option Codes for Equation of State Models in *Physical Property Models* for information about other option codes.

For more information on the SRK package, see Aspen HYSYS help.

MXBONNEL

The MXBONNEL property method uses the:

- Ideal gas for vapor fugacity coefficients
- Maxwell-Bonnell model for vapor pressure to compute liquid fugacity coefficient (K-Values)
- Soave-Redlich-Kwong equation of state for liquid and vapor phase properties. Water enthalpy calculated from NBS steam tables.
- TRAPP model for transport properties

This method is similar to the BK10 method, except that Maxwell-Bonnell vapor pressure method is used for all hydrocarbon pseudo-components. For pure components, their standard vapor pressure correlation is used. This method should only be used in low pressure (below a few atmospheres) applications.

Mixture Types

The MXBONNEL property method can be used for crude towers, vacuum towers, and some parts of the ethylene process. Best results are obtained for mixture of hydrocarbons. For mixtures with light gases and medium pressures, CHAO-SEA or GRAYSON is recommended.

Range

The MXBONNEL property method is suited for vacuum and low pressure applications (up to several atmospheres). Do not use this property method at very high pressures, especially near the mixture critical point, because of anomalous behavior in these regions.

The SRK property method uses the Soave-Redlich-Kwong (SRK) cubic equation of state for all thermodynamic properties with option to improve liquid molar volume using volume correction.

This method has the following options:

- Peneloux-Rauzy method for liquid molar volume correction which results in more accurate liquid molar volume
- NBS Steam Table for calculating properties of water for better accuracy
- Kabadi-Danner mixing rules when dealing with water-hydrocarbon systems (See SRK-KD)
- Composition-independent fugacity coefficient for faster convergence in equation-based modeling
- Modified l_{ij} parameters in the SRK-ML model.

When using the SRK method, please select STEAMNBS as the free-water method. The NBS steam table provides greater accuracy and SRK is designed to work with it. The enthalpy, entropy, Gibbs energy, and molar volume of water are calculated from the steam tables. The total properties are mole-fraction averages of these values with the properties calculated by the equation of state for other components. Fugacity coefficient is not affected.

Refer to the tables labeled Parameters Required for the SRK Property Method below and Parameters Required for Common Models for thermodynamic and transport property models, and required parameters for this property method.

This property method is comparable to other property methods based on cubic equations of state. It is recommended for gas-processing, refinery, and petrochemical applications. Example applications include gas plants, crude towers, and ethylene plants.

The SRK property method has built-in pure component and binary parameters for use in modeling the ethylene process. The built-in parameters are stored in the databank. For other systems, you must supply pure component and binary parameters. You can use the Data Regression System (DRS) to determine the binary parameters from experimental phase equilibrium data (binary VLE and LLE data).

Mixture Types

Use the SRK property method for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen. For systems with polar components, such as alcohols, use the SR-POLAR, WILSON, NRTL, VANLAAR, or UNIQUAC property methods, or specify values for the l_{ij} parameters. This property method is particularly suitable in the high temperature and high pressure regions, such as in hydrocarbon processing applications or supercritical extractions.

With the Kabadi-Danner mixing rules, this property method can be used to model water-hydrocarbon immiscibility.

Range

You can expect reasonable results at all temperatures and pressures. The SRK property method is consistent in the critical region. Therefore, unlike the activity coefficient property methods, it does not exhibit anomalous behavior. Results are least accurate in the region near the mixture critical point.

Parameters Required for the SRK Property Method

Thermodynamic Properties	**Models**	**Parameter Requirements**
Vapor mixture Fugacity coefficient, Density	Soave-Redlich-Kwong	SRKTC, SRKPC, SRKOMG

Thermodynamic Properties	Models	Parameter Requirements
Enthalpy, entropy Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Soave-Redlich-Kwong	SRKTC, SRKPC, SRKOMG
Liquid mixture Fugacity coefficient, Density	Soave-Redlich-Kwong	SRKTC, SRKPC, SRKOMG
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Soave-Redlich-Kwong	SRKTC, SRKPC, SRKOMG

RTOMXB

The RTOMXB method is an old version of MXBONNEL, intended for use only with legacy RT-Opt projects which have been tuned to use this method.

Petroleum-Tuned Equation-of-State Property Methods

Petroleum-tuned equation-of-state property methods are based on equations of state for nonpolar compounds with built-in binary parameters. These property methods use the API/Rackett model for liquid density to overcome the drawback of poor liquid density calculated by cubic equations of state. Liquid viscosity and surface tensions are calculated by API models.

Equations of state are comparable in performance when comparing VLE. BWR-LS is recommended for hydrogen-rich systems.

Property methods based on liquid fugacity correlations or K-value models are generally preferred for low pressure refinery applications. Petroleum-tuned equation-of-state models can handle critical points, but some other models of the property methods (such as liquid density and liquid viscosity) are not suited for conditions close to criticality, as occur in light oil reservoirs, transportation of gas by pipe lines, and in some gas processing applications. For these cases, equation-of-state property methods for high pressure hydrocarbon applications are preferred. If polar compounds are present, such as in gas treatment, use flexible and predictive equations of state for polar compounds.

PENG-ROB

The PENG-ROB property method uses the:

- Standard Peng-Robinson cubic equation of state for all thermodynamic properties except liquid molar volume

- API method for liquid molar volume of pseudocomponents and the Rackett model for real components

Refer to the tables labeled Parameters Required for the PENG-ROB Property Method (below) and Parameters Required for Common Models for thermodynamic and transport property models, and their required parameters.

This property method is comparable to the RK-SOAVE property method. It is recommended for gas-processing, refinery, and petrochemical applications. Sample applications include gas plants, crude towers, and ethylene plants.

For accurate results in your VLE or LLE calculations, you must use binary parameters, such as the Aspen Physical Property System built-in binary parameters. Use the **Methods | Parameters | Binary Interaction | PRKBV** form to review available built-in binary parameters. You can also use the Data Regression System (DRS) to determine the binary parameters from experimental phase equilibrium data (usually binary VLE data).

By default, this property method uses the literature version of the alpha function and mixing rules (D.-Y. Peng and D. B. Robinson, "A New Two-Constant Equation-of-state," *Ind. Eng. Chem. Fundam.*, Vol. 15, (1976), pp. 59–64). However, the Peng-Robinson model has been extended to handle polar components and non-ideal chemical systems as described in the property model description.

Mixture Types

Use the PENG-ROB property method for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen. For systems with polar components, use the SR-POLAR, PRWS, RKSWS, PRMHV2, RKSMHV2, PSRK, WILSON, NRTL, VANLAAR, or UNIQUAC property methods.

This property method is particularly suitable in the high temperature and high pressure regions, such as in hydrocarbon processing applications or supercritical extractions.

This property method can be used for polar, non-ideal chemical mixtures, if appropriate alpha functions and mixing rules are used. Please refer to the description of the Peng-Robinson model in the property model description.

Range

You can expect reasonable results at all temperatures and pressures. The PENG-ROB property method is consistent in the critical region. Therefore, it does not exhibit anomalous behavior, unlike the activity coefficient property methods. Results are least accurate in the region near the mixture critical point.

Parameters Required for the PENG-ROB Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient Density	Peng-Robinson	TCPR or TC; PCPR or PC; OMGPR or OMEGA
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Peng-Robinson	TCPR or TC; PCPR or PC; OMGPR or OMEGA
Liquid mixture Fugacity coefficient	Peng-Robinson	TCPR or TC; PCPR or PC; OMGPR or OMEGA CPIG or CPIGDP
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Peng-Robinson	TCPR or TC; PCPR or PC; OMGPR or OMEGA

RK-SOAVE

The RK-SOAVE property method uses the:

- Redlich-Kwong-Soave (RKS) cubic equation of state for all thermodynamic properties except liquid molar volume
- API method for liquid molar volume of pseudocomponents and the General model for real components

Refer to the tables labeled Parameters Required for the RK-SOAVE Property Method (below) and Parameters Required for Common Models for thermodynamic and transport property models, and required parameters for this property method.

This property method is comparable to the PENG-ROB property method. It is recommended for gas-processing, refinery, and petrochemical applications. Example applications include gas plants, crude towers, and ethylene plants. The RK-SOAVE property method has built-in binary parameters, RKSKBV, that are used automatically in the Aspen Physical Property System.

For accurate results in your VLE and LLE calculations, you must use binary parameters. You can use the Aspen Physical Property System built-in parameters. Use the **Methods | Parameters | Binary Interaction | RKSKBV-1** form to review available built-in binary parameters. You can also use the Data Regression System (DRS) to determine the binary parameters from experimental phase equilibrium data (usually binary VLE data).

Mixture Types

Use the RK-SOAVE property method for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen. For systems with polar components, such as alcohols, use the SR-POLAR, WILSON, NRTL, VANLAAR, or UNIQUAC property methods.

This property method is particularly suitable in the high temperature and high pressure regions, such as in hydrocarbon processing applications or supercritical extractions.

Range

You can expect reasonable results at all temperatures and pressures. The RK-SOAVE property method is consistent in the critical region. Therefore, unlike the activity coefficient property methods, it does not exhibit anomalous behavior. Results are least accurate in the region near the mixture critical point.

Parameters Required for the RK-SOAVE Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Redlich-Kwong-Soave	TC, PC, OMEGA
Enthalpy, entropy Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Redlich-Kwong-Soave	TC, PC, OMEGA
Liquid mixture Fugacity coefficient	Redlich-Kwong-Soave	TC, PC, OMEGA
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity,	CPIG or CPIGDP
	Redlich-Kwong-Soave	TC, PC, OMEGA

SRK

The SRK property method uses the Soave-Redlich-Kwong (SRK) cubic equation of state for all thermodynamic properties with option to improve liquid molar volume using volume correction.

This method has the following options:

- Peneloux-Rauzy method for liquid molar volume correction which results in more accurate liquid molar volume
- NBS Steam Table for calculating properties of water for better accuracy
- Kabadi-Danner mixing rules when dealing with water-hydrocarbon systems (See SRK-KD)

- Composition-independent fugacity coefficient for faster convergence in equation-based modeling
- Modified l_{ij} parameters in the SRK-ML model.

When using the SRK method, please select STEAMNBS as the free-water method. The NBS steam table provides greater accuracy and SRK is designed to work with it. The enthalpy, entropy, Gibbs energy, and molar volume of water are calculated from the steam tables. The total properties are mole-fraction averages of these values with the properties calculated by the equation of state for other components. Fugacity coefficient is not affected.

Refer to the tables labeled Parameters Required for the SRK Property Method below and Parameters Required for Common Models for thermodynamic and transport property models, and required parameters for this property method.

This property method is comparable to other property methods based on cubic equations of state. It is recommended for gas-processing, refinery, and petrochemical applications. Example applications include gas plants, crude towers, and ethylene plants.

The SRK property method has built-in pure component and binary parameters for use in modeling the ethylene process. The built-in parameters are stored in the databank. For other systems, you must supply pure component and binary parameters. You can use the Data Regression System (DRS) to determine the binary parameters from experimental phase equilibrium data (binary VLE and LLE data).

Mixture Types

Use the SRK property method for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen. For systems with polar components, such as alcohols, use the SR-POLAR, WILSON, NRTL, VANLAAR, or UNIQUAC property methods, or specify values for the l_{ij} parameters. This property method is particularly suitable in the high temperature and high pressure regions, such as in hydrocarbon processing applications or supercritical extractions.

With the Kabadi-Danner mixing rules, this property method can be used to model water-hydrocarbon immiscibility.

Range

You can expect reasonable results at all temperatures and pressures. The SRK property method is consistent in the critical region. Therefore, unlike the activity coefficient property methods, it does not exhibit anomalous behavior. Results are least accurate in the region near the mixture critical point.

Parameters Required for the SRK Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Soave-Redlich-Kwong	SRKTC, SRKPC, SRKOMG
Enthalpy, entropy Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Soave-Redlich-Kwong	SRKTC, SRKPC, SRKOMG
Liquid mixture Fugacity coefficient, Density	Soave-Redlich-Kwong	SRKTC, SRKPC, SRKOMG
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Soave-Redlich-Kwong	SRKTC, SRKPC, SRKOMG

RTOSRK

RTOSRK is an older version of SRK, intended for use only with legacy RT-Opt projects which were tuned to use this method. In these circumstances it is used together with RTOSTM for free water.

SRK-KD

The SRK-KD property method uses the SRK-Kabadi-Danner property model. This is equivalent to the SRK property method with the Kabadi-Danner mixing rules included.

The Kabadi-Danner mixing rules allow this property method to model water-hydrocarbon immiscibility. These special mixing rules handle the interaction between water and hydrocarbon components. The interaction is accounted for by the use of a binary interaction parameter which can be estimated from group contribution.

Do not use the SRK l_{ij} parameters with the Kabadi-Danner mixing rules. Both these methods model the asymmetric behavior of polar-hydrocarbon interactions, but they are not designed to be used simultaneously.

SRK-ML

The SRK-ML property method uses the SRK-ML property model. This is equivalent to the SRK property method with an alternate set of k_{ij} parameters, and l_{ij} based on the k_{ij}.

Common Models for Property Methods for Petroleum Mixtures

The following table lists the models used in all petroleum property methods and their parameter requirements.

Parameters Required for Common Models

General

Property/Purpose	Parameter Requirements
Mass balance, Conversion Mass-basis↔ Mole-basis	MW
Conversion Stdvol-basis↔ Mole-basis	VLSTD
Initialization of Flash calculations	PLXANT
Using Free-water option: solubility of water in organic phase	WATSOL
Enthalpy, enthalpy of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Thermodynamic Properties

Property	Models	Parameter Requirements
Liquid mixture Enthalpy, Entropy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Lee-Kesler	TC, PC, OMEGA
Density	Real components: General Pure Component Liquid Molar Volume	TC, PC, (VC or VCRKT), (ZC or RKTZRA)
	Pseudo components: API	TB, API

Transport Properties

Property	Models	Paremeter Requirements
Vapor mixture Viscosity	General Pure Component Vapor Viscosity	MW, (MUP and (STKPAR or LJPAR)) or MUVDIP

Property	Models	Paremeter Requirements
Thermal Conductivity	General Pure Component Vapor Thermal Conductivity	MW or KVDIP (and vapor viscosity parameters)
Diffusivity	Dawson Khoury-Kobayashi	MW, MUP, (STKPAR or LJPAR), VC
Liquid mixture Viscosity	API	TB, API
Thermal Conductivity	General Pure Component Liquid Thermal Conductivity	(MW, TB, TC) or KLDIP
Diffusivity	Wilke-Chang	MW, VB
Surface tension	API	TB, TC, SG

Equation-of-State Property Methods for High-Pressure Hydrocarbon Applications

The following table, Equation of State Property Methods for Hydrocarbons at High Pressure, lists property methods for mixtures of hydrocarbons and light gases. The property methods can deal with high pressures and temperatures, and mixtures close to their critical point (for example, pipeline transportation of gas or supercritical extraction). All thermodynamic properties of vapor and liquid phases are calculated from the equations of state. (See Equation of State Method in Overview of Aspen Physical Property Methods). The TRAPP models for viscosity and thermal conductivity can describe the continuity of gas and liquid beyond the critical point, comparable to an equation of state.

The hydrocarbons can be from complex crude or gas mixtures treated using pseudocomponents. But the property methods for petroleum mixtures are better tuned for these applications at low to medium pressures. Unless you use fitted binary interaction parameters, no great accuracy should be expected close to the critical point. Liquid densities are not accurately predicted for the cubic equations of state.

In the presence of polar components (for example, in gas treatment), flexible and predictive equations of state should be used. For mixtures of polar and nonpolar compounds at low pressures, use an activity-coefficient-based property method.

The following table lists the common and distinctive models of the property methods BWR-LS, LK-PLOCK, PR-BM, and RKS-BM. The parameter requirements of the common models are given in the table labeled Parameters Required for Common Models. The parameter requirements for the distinctive models are in the tables labeled Parameters Required for the BWR-LS Property Method (see BWR-LS) , Parameters Required for the BWRS Property Method (see BWRS) , Parameters Required for the LK-PLOCK Property Method (see LK-PLOCK) , Parameters Required for the PR-BM Property Method (see PR-BM) , and Parameters Required for the RKS-BM Property Method (see RKS-BM) .

Equation-of-State Property Methods for Hydrocarbons at High Pressure

Property Method Name	Models
BWR-LS	BWR-Lee-Starling
BWRS	Benedict-Webb-Rubin-Starling
LK-PLOCK	Lee-Kesler-Plöcker
PR-BM	Peng-Robinson-Boston-Mathias
RKS-BM	Redlich-Kwong-Soave-Boston-Mathias

Property	Common Models
Vapor viscosity	TRAPP
Vapor thermal conductivity	TRAPP
Vapor diffusivity	Dawson-Khoury-Kobayashi
Surface tension	API surface tension
Liquid viscosity	TRAPP
Liquid thermal conductivity	TRAPP
Liquid diffusivity	Wilke-Chang

BWR-LS

The BWR-LS property method is based on the BWR-Lee-Starling equation of state. It is the generalization (in terms of pure component critical properties) of the Benedict-Webb-Rubin virial equation of state. The property method uses the equation of state for all thermodynamic properties. Refer to the table Parameters Required for the BWR-LS Property Method (below) and Parameters Required for Common Models for thermodynamic and transport property models and their parameter requirements.

The BWR-LS property method is comparable to PENG-ROB, RK-SOAVE, and LK-PLOCK for phase equilibrium calculations, but is more accurate than PENG-ROB and RK-SOAVE for liquid molar volume and enthalpy. You can use it for gas processing and refinery applications. It is suited for hydrogen-containing systems, and has shown good results in coal liquefaction applications.

For accurate results, use the binary interaction parameters. Built-in binary parameters BWRKV and BWRKT are available for a large number of component pairs. The Aspen Physical Property System uses these binary parameters automatically. Use the **Methods| Parameters | Binary Interaction | BWRKV-1** and **BWRKT-1** forms to review available built-in binary parameters. You can also use the Data Regression System (DRS) to determine the binary parameters from experimental phase equilibrium data (usually binary VLE data).

Mixture Types

Use the BWR-LS property method for nonpolar or slightly polar mixtures, and light gases. Asymmetric interactions between long and short molecules are well predicted.

Range

You can expect reasonable results up to medium pressures. At very high pressures, unrealistic liquid-liquid demixing may be predicted. High pressure liquid-liquid demixing occurs between short and long chain hydrocarbons and also, for example, between carbon dioxide and longer hydrocarbon chains at high pressures.

Parameters Required for the BWR-LS Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	BWR-Lee-Starling	TC, VC, OMEGA
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	BWR-Lee-Starling	TC, VC, OMEGA
Liquid mixture Fugacity coefficient, Density	BWR-Lee-Starling	TC, VC, OMEGA
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	BWR-Lee-Starling	TC, VC, OMEGA

BWRS

The BWRS property method is based on the Benedict-Webb-Rubin-Starling equation of state with optional pure-component and binary interaction parameters. This equation has eleven pure-component parameters along with binary interaction parameters. These parameters are obtained from multiproperty (vapor-liquid-equilibrium, enthalpy, PVT, etc.) data regressions. Parameters for chemicals common to natural gas mixtures are available from Starling (1973). If pure-component parameters are not supplied, they are estimated with correlations proposed by Starling. The property method uses the equation of state for all thermodynamic properties. Refer to the table labeled Parameters Required for the BWRS Property Method (below) and Parameters Required for Common Models for thermodynamic and transport property models and their parameter requirements.

The BWRS property method is comparable to PENG-ROB, RK-SOAVE, BWR-LS and LK-PLOCK for phase equilibrium calculations, but is more accurate than PENG-ROB and RK-SOAVE for liquid molar volume and enthalpy. You can use it for gas processing and refinery applications. It is suited for reduced temperatures as low as T_r = 0.3 and reduced densities as great as ρ_r = 3.0. It can be used for light hydrocarbons in the cryogenic liquid region in addition to higher temperature regions.

For accurate results, use the binary interaction parameters. The Aspen Physical Property System does not have built-in binary parameters. You can use the Data Regression System (DRS) to determine the binary parameters from experimental phase equilibrium data (usually binary VLE data).

The BWRS method is suitable when you need very high accuracy in pure component properties. When good parameter values are given, this method can calculate very accurate properties (vapor pressure, molar volume, and enthalpy) for pure components. The model is also very good for light hydrocarbon systems and light gases such as N2, CO2, and H2S when the binary parameters are given.

When water is present, by default BWRS uses the steam table to calculate the enthalpy, entropy, Gibbs energy, and molar volume of water. The total properties are mole-fraction averages of these values with the properties calculated by the equation of state for other components. Fugacity coefficient is not affected. An option code can disable this use of the steam table.

Note: When using BWRS, make sure to add the **AP V120 EOS-LIT** databank to the **Selected databanks** list.

Mixture Types

Use the BWRS property method for non-polar or slightly polar mixtures, and light gases. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and nitrogen.

Range

You can expect reasonable results at all temperatures and pressures. The BWRS property method is consistent in the critical region. It does not exhibit anomalous behavior, unlike the activity coefficient property methods. Results are least accurate in the region near the mixture critical point.

Parameters Required for the BWRS Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Benedict-Webb-Rubin-Starling	BWRSTC, BWRSVC, BWRSOM
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Benedict-Webb-Rubin-Starling	BWRSTC, BWRSVC, BWRSOM
Liquid mixture Fugacity coefficient, Density	Benedict-Webb-Rubin-Starling	BWRSTC, BWRSVC, BWRSOM
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity,	CPIG or CPIGDP
	Benedict-Webb-Rubin-Starling	BWRSTC, BWRSVC, BWRSOM

Reference: K. E. Starling, "Fluid Thermodynamic Properties for Light Petroleum Systems", Gulf Publishing Co., Houston, Texas (1973).

LK-PLOCK

The LK-PLOCK property method is based on the Lee-Kesler-Plöcker equation of state, which is a virial-type equation. LK-PLOCK uses the:

- EOS to calculate all thermodynamic properties except liquid molar volume of mixtures
- API method for liquid molar volume of pseudocomponents and the Rackett model for real components, in mixtures

You can use LK-PLOCK for gas-processing and refinery applications, but the RK-SOAVE or the PENG-ROB property methods are preferred.

Refer to the tables labeled Parameters Required for the LK-PLOCK Property Method (below) and Parameters Required for Common Models for thermodynamic and transport property models, and their parameter requirements.

For accurate results in VLE calculations, use binary parameters. Built-in binary parameters LKPKIJ are available for a large number of component pairs. The Aspen Physical Property System uses these binary parameters automatically. Use the **Methods | Parameters | Binary Interaction | LKPKIJ-1** form to review available built-in binary parameters. You can also use the Data Regression System (DRS) to determine the binary parameters from experimental phase equilibrium data (usually binary VLE data).

This property method also has built-in correlations for estimating binary parameters among the components CO, CO_2, N_2, H_2, CH_4, alcohols, and hydrocarbons. Components not belonging to the classes listed above are assumed to be hydrocarbons.

Mixture Types

Use the LK-PLOCK property method for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen.

Range

You can expect reasonable results at all temperatures and pressures. The LK-PLOCK property method is consistent in the critical region. It does not exhibit anomalous behavior, unlike the activity coefficient property methods. Results are least accurate in the region near the mixture critical point.

Parameters Required for the LK-PLOCK Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Lee-Kesler-Plöcker	TC, PC, VC, OMEGA
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Lee-Kesler-Plöcker	TC, PC, VC, OMEGA
Liquid mixture Fugacity coefficient	Lee-Kesler-Plöcker	TC, PC, VC, OMEGA
Density	Rackett/API	TB, API, TC, PC, RKTZRA
Enthalpy, entropy Gibbs free energy	General pure component ideal gas heat capacity,	CPIG or CPIGDP
	Lee-Kesler-Plöcker	TC, PC, VC, OMEGA

PR-BM

The PR-BM property method uses the Peng Robinson cubic equation of state with the Boston-Mathias alpha function for all thermodynamic properties.

Refer to the tables labeled Parameters Required for the PR-BM Property Method (below) and Parameters Required for Common Models for thermodynamic and transport property models, and their required parameters.

This property method is comparable to the RKS-BM property method. It is recommended for gas-processing, refinery, and petrochemical applications. Sample applications include gas plants, crude towers, and ethylene plants.

For accurate results in your VLE calculations, you must use binary parameters. The Aspen Physical Property System does not have built-in binary parameters for this property method.

Mixture Types

Use the PR-BM property method for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen.

Range

You can expect reasonable results at all temperatures and pressures. The PR-BM property method is consistent in the critical region. Results are least accurate in the region near the mixture critical point.

Parameters Required for the PR-BM Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor or liquid mixture Fugacity coefficient, Density	Peng-Robinson	TCPR, PCPR, OMEGA
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Peng-Robinson	TCPR, PCPR, OMEGA

RKS-BM

The RKS-BM property method uses the Redlich-Kwong-Soave (RKS) cubic equation of state with Boston-Mathias alpha function for all thermodynamic properties.

This property method is comparable to the PR-BM property method. It is recommended for gas-processing, refinery, and petrochemical applications. Example applications include gas plants, crude towers, and ethylene plants.

For accurate results in your VLE calculations, you must use binary parameters. The binary parameters available are automatically retrieved from the EOS-LIT databank.

Mixture Types

Use the RKS-BM property method for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen.

Range

You can expect reasonable results at all temperatures and pressures. The RKS-BM property method is consistent in the critical region. Results are least accurate in the region near the mixture critical point.

Refer to the tables labeled Parameters Required for the RKS-BM Property Method (below) and Parameters Required for Common Models for thermodynamic and transport property models, and their required parameters.

Parameters Required for the RKS-BM Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor or liquid mixture Fugacity coefficient, Density	Redlich-Kwong-Soave	TCRKS, PCRKS, OMGRKS
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Redlich-Kwong-Soave	TCRKS, PCRKS, OMGRKS

Common Models for Equation-of-State Property Methods for High-Pressure Hydrocarbon Applications

The following table lists the models common to equation-of-state property methods for high–pressure hydrocarbon applications and their parameter requirements.

Parameters Required for Common Models

General

Property/Purpose	Parameter Requirements
Mass balance, Conversion Mass-basis↔ Mole-basis	MW
Conversion Stdvol-basis↔ Mole-basis	VLSTD
Initialization of Flash calculations	PLXANT
Using Free-water option: solubility of water in organic phase	WATSOL
Enthalpy, enthalpy of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Transport

Property	Models	Parameter Requirements
Vapor Mixture Viscosity	TRAPP	TC, PC, OMEGA
Thermal Conductivity	TRAPP	TC, PC, OMEGA
Diffusivity	Dawson-Khoury-Kobayashi	MW, MUP, (STKPAR or LJPAR), VC
Surface tension	API	TB, TC, SG
Liquid mixture Viscosity	TRAPP	TC, PC, OMEGA
Thermal Conductivity	TRAPP	TC, PC, OMEGA
Diffusivity	Wilke-Chang	MW, VB

Flexible and Predictive Equation-of-State Property Methods

The table labeled Flexible and Predictive Equation-of-State Property Methods (below) lists property methods for mixtures of polar and non-polar components and light gases. The property methods can deal with high pressures and temperatures, mixtures close to their critical point, and liquid-liquid separation at high pressure. Examples of applications are gas drying with glycols, gas sweetening with methanol, and supercritical extraction.

Pure component thermodynamic behavior is modeled using the Peng-Robinson or Redlich-Kwong-Soave equations of state. They are extended with flexible alpha-functions with up to three parameters, for very accurate fitting of vapor pressures. This is important in separations of very closely boiling systems and for polar compounds. In some cases they are extended with a volume translation term for accurate fitting of liquid densities (see the table labeled Flexible and Predictive Equation-of-State Property Methods below).

Parameters for the Schwartzentruber-Renon and Mathias-Copeman alpha functions are available for many components in the PURECOMP databank.

Mixing rules for these models vary. Extended classical mixing rules are used for fitting hydrogen-rich systems or systems with strong size and shape asymmetry (Redlich-Kwong-Aspen). Composition and temperature-dependent mixing rules fit strongly non-ideal high pressure systems (SR-POLAR). Modified Huron-Vidal mixing rules can predict non-ideality at high pressure from low-pressure (group-contribution) activity coefficient models (Wong-Sandler, MHV2, PSRK). The predictive capabilities of modified Huron-Vidal mixing rules are superior to the predictive capabilities of SR-POLAR. The differences among capabilities of the modified Huron-Vidal mixing rules are small (see *Physical Property Models*).

The Wong-Sandler, MHV2, and Holderbaum-Gmehling mixing rules use activity coefficient models to calculate excess Gibbs or Helmholtz energy for the mixing rules. The property methods with these mixing rules use the UNIFAC or Lyngby modified UNIFAC group contribution models. Therefore, they are predictive. You can use any Aspen Physical Property System activity coefficient models with these mixing rules, including user models. Use the Properties Methods Models sheet to modify the property method. See Modifying and Creating Property Methods for details on how to modify a property method.

The Chung-Lee-Starling models for viscosity and thermal conductivity can describe the continuity of gas and liquid beyond the critical point. This is comparable to an equation of state. These models can fit the behavior of polar and associating components. Details about the pure component models and mixing rules are found in *Physical Property Models*.

For mixtures of polar and non-polar compounds at low pressures, activity coefficient models are preferred. For non-polar mixtures of petroleum fluids and light gases at low to medium pressures, the property methods for petroleum mixtures are recommended. The flexible and predictive equations of state are not suited for electrolyte solutions.

The following table, Flexible and Predictive Equation-of-State Property Methods, lists flexible and predictive equation-of-state property methods, the distinctive equation-of-state models on which they are based, and some of their characteristics. The table also gives the models that the property methods have in common. Parameter requirements of the common models are given in the table labeled Parameters Required for Common Flexible and Predictive Models. Parameter requirements for the distinctive models are in the tables labeled Parameters Required for the PRMHV2 Property Method (see PRMHV2), Parameters Required for the PRWS Property Method (see PRWS), Parameters Required for the PSRK Property Method (see PSRK), Parameters Required for the RK-ASPEN Property Method (RK-ASPEN), Parameters Required for the RKSMHV2 Property Method (see RKSMHV2), Parameters Required for the RKSWS Property Method (see RKSWS), and Parameters Required for the SR-POLAR Property Method (see SR-POLAR).

Flexible and Predictive Equation-of-State Property Methods

Property Method Name	Equation of State	Volume Shift	Mixing Rule	Predictive
HYSGLYCO	Twu-Sim-Tassone	—	—	X
PC-SAFT	Copolymer PC-SAFT	—	—	—
PRMHV2	Peng-Robinson	—	MHV2	X
PRWS	Peng-Robinson	—	Wong-Sandler	X
PSRK	Redlich-Kwong-Soave	—	Holderbaum-Gmehling	X
RK-ASPEN	Redlich-Kwong-Soave	—	Mathias	—
RKSMHV2	Redlich-Kwong-Soave	—	MHV2	X
RKSWS	Redlich-Kwong-Soave	—	Wong-Sandler	X
SR-POLAR	Redlich-Kwong-Soave	X	Schwarzentruber-Renon	—

An X in the Volume Shift column indicates volume shift is included in the property method.

An X in the Predictive column indicates that the property method is predictive.

Property	Common Models
Vapor viscosity	Chung-Lee-Starling
Vapor thermal conductivity	Chung-Lee-Starling
Vapor diffusivity	Dawson-Khoury-Kobayashi

Property	Common Models
Surface tension	General Pure Component Liquid Surface Tension
Liquid viscosity	Chung-Lee-Starling
Thermal conductivity	Chung-Lee-Starling
Liquid diffusivity	Wilke-Chang liquid

CPA

The CPA method represents the Cubic-Plus-Association EOS model developed by Kontogeorgis and co-workers (Kontogeorgis, Voutsas, Yakoumis, Tassios, IECR 1996). The model combines the SRK cubic EOS with an association term similar to that of SAFT, as present in the PC-SAFT model. Mixing rules apply to the cubic, whereas combining rules are used for the association term. The model's applicability covers the VLE and VLLE of mixtures containing hydrocarbons and polar/associating chemicals such as water, alcohols, glycols, esters, and organic acids.

The CPA (Cubic-Plus-Association) property method uses the Soave-Redlich-Kwong (SRK) cubic equation of state combined with the association term for SAFT for all thermodynamic properties.

Refer to the tables labeled Parameters Required for the CPA Property Method below and Parameters Required for Common Models for thermodynamic and transport property models, and required parameters for this property method.

In the absence of associating (hydrogen-bonding) species, this property method reduces to the SRK model, widely used for gas-processing, refinery, petrochemical applications. The addition of the association term for components capable of exhibiting hydrogen-bonding (water, alcohols, glycols, acids) enables CPA to better model the V(L)LE of complex systems.

The CPA property method has built-in pure component and binary parameters for use in modeling processes such as Methanol gas cleaning. The built-in parameters are stored in the AP-EOS databank. For species not in the databank, Aspen Properties will estimate the non-associating pure component parameters from the critical temperature, critical pressure, and acentric factor. We recommend however, and necessary for associating components, that you use the Data Regression System (DRS) to determine the pure component parameters from vapor pressure and liquid density data, and the binary parameters from experimental phase equilibrium data (binary VLE and LLE data).

Mixture Types

Use the CPA property method for nonpolar or associating mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen. For systems with associating (polar) components, such as alcohols, specify values for the association parameters if not present in AP-EOS.. This property method is particularly suitable in the high temperature and high pressure regions, such as in hydrocarbon processing applications or supercritical extractions.

Range

You can expect reasonable results at all temperatures and pressures. The CPA property method is consistent in the critical region. Therefore, unlike the activity coefficient property methods, it does not exhibit anomalous behavior. Results are least accurate in the region near the mixture critical point.

Parameters Required for the CPA Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture		
Fugacity coefficient, Density	CPA	CPATC, CPAPC, CPAM CPAAU, CPAAV (associating)
Enthalpy, entropy Gibbs free energy	General pure component ideal gas heat capacity, CPA	(CPIG or CPIGDP) and CPATC, CPAPC, CPAM CPAAU, CPAAV (associating)
Liquid mixture		
Fugacity coefficient, Density	CPA	CPATC, CPAPC, CPAM CPAAU, CPAAV (associating)
Enthalpy, entropy, Gibbs free energy	General pure component ideal gas heat capacity, CPA	(CPIG or CPIGDP) and CPATC, CPAPC, CPAM CPAAU, CPAAV (associating)

HYSGLYCO

The HYSGLYCO property method implements the Glycol property package from Aspen HYSYS. It uses the TST (Twu-Sim-Tassone) equation of state to determine the phase behaviour more accurately and consistently for the TEG-water mixture. The property package contains the necessary pure component and binary interaction parameters for components commonly encountered in natural gas dehydration process. The property package is tuned to represent accurately, the phase behaviour of these components, especially that for the TEG-water binary system.

The TST equation of state can accurately predict:

- activity coefficients of the TEG-water solutions within the average absolute deviation of 2%
- dew point temperatures within an average error of ±1°C.
- water content of gas within the average absolute deviation of 1%

The Glycol property package should be applicable over the range of temperatures, pressures, and component concentration encountered in a typical TEG-water dehydration system: between 15°C to 50°C and between 10 atm to 100 atm for the gas dehydrator, and between 202°C to 206°C and 1.2 atmospheres for the glycol regenerator.

The accuracy of predicted solubility of hydrocarbons in aqueous phase is expected to be within the experimental uncertainty.

The table below displays the prediction of equilibrium water content in lbH2O/MMSCF for a gas stream in contact with 99.5 weight percent TEG, using the Glycol property package.

T dew (K)	**Reported by:**		**Predicted from TST (EOS):**	
	McKetta	**Bukacek**	**Water Content**	**Pressure (Pa)**
277.59	390	396	393	838
266.48	170	176	174	370
255.37	70	72	71	151
244.26	28	27	26	56.1
233.15	9.2	9.1	9	18.7
222.04	2.4	2.8	2.6	6

The BIP databank for the Glycol property package is continuously updated. Currently, there may be some limitations or missing BIP for certain component pairs. For example, heavy hydrocarbons or hypothetical components which may not have any interaction parameters available.

Glycol Calculation Methods

For the Glycol property package, three alpha function parameters are used to correlate the vapor pressure of the component in the HYSYS component databank. The alpha function parameters are: L, M, and N parameters that are unique for each component.

For Glycol property package, three adjustable parameters are used to correlate Vapor-Liquid-Equilibrium (VLE) mixture data. The parameters corresponding to the TST (Twu-Sim-Tassone) AE mixing rules are A_{ij}, A_{ji}, and α_{ij} binary interaction parameters in the NRTL equation. The Glycol property package uses the Cavett model for enthalpy and entropy calculations.

Parameters used by the HYSGLYCO property method:

- GLYABV: Glycol EOS activity binary parameters A_{ij}, B_{ij} and C_{ij}
- GLYKIJ: Glycol EOS binary parameter
- GLYLMN: Parameters for the Twu Alpha function
- PCGLY: Critical pressure
- TCGLY: Critical temperature

These parameters and others used by HYSGLYCO are available in the HYSYS databank. When using HYSGLYCO it is recommended to place the HYSYS databank in the search order before other databanks.

The liquid thermal conductivity model uses API methods rather than the HYSYS model for pseudocomponents:

- API equation 12A3.2-1 for normal boiling point T_b above 337 K
- API equation 12A1.2-1 for other components with molecular weight above 140 and reduced temperature $T_r=T/T_c$ below 0.8

With option code 1 set to 1 in KL2GLY and KL0GLY, API equation 12A1.2-1 is used for all components.

Option code 1 of ESGLY and ESGLY0 controls the volume root search method. The default is 0, to use an analytical solution. This analytical solution may produce a wrong root in some cases, such as with some pure water streams. If you get results showing the wrong phase with HYSGLYCO and such streams, change this option code to 1 to use the numerical solution. See Option Codes for Equation of State Models in *Physical Property Models* for information about other option codes.

For more information on the Glycol package, see Aspen HYSYS help.

PC-SAFT: Copolymer PC-SAFT EOS Property Method

The PC-SAFT method represents the copolymer PC-SAFT EOS model developed by Sadowski and co-workers (Gross and Sadowski, 2001, 2002a, 2002b; Gross et al., 2003; Becker et al., 2004; Kleiner et al., 2006). Unlike the POLYPCSF method, the copolymer PC-SAFT includes the association and polar terms and does not apply mixing rules to calculate the copolymer parameters from its segments. Its applicability covers fluid systems from small to large molecules, including normal fluids, water, alcohols, and ketones, polymers and copolymers and their mixtures.

The following table lists the physical property route structure for the PC-SAFT property method:

Vapor

Property Name	Route ID	Model Name	Description
PHIVMX	PHIVMXPA	ESPSAFT	Copolymer PCSAFT
HVMX	HVMXPA	ESPSAFT	Copolymer PCSAFT
GVMX	GVMXPA	ESPSAFT	Copolymer PCSAFT
SVMX	SVMXPA	ESPSAFT	Copolymer PCSAFT
VVMX	VVMXPA	ESPSAFT	Copolymer PCSAFT
MUVMX	MUVMX02	MUV2DNST	Dean-Stiel
KVMX	KVMX02	KV2STLTH	General Pure Component Vapor Thermal Conductivity
DVMX	DVMX02	DV1DKK	Dawson-Khoury-Kobayashi
PHIV	PHIVPA	ESPSAFT0	Copolymer PCSAFT
HV	HVPA	ESPSAFT0	Copolymer PCSAFT
GV	GVPA	ESPSAFT0	Copolymer PCSAFT
SV	SVPA	ESPSAFT0	Copolymer PCSAFT
VV	VVPA	ESPSAFT0	Copolymer PCSAFT
DV	DV01	DV0CEWL	Chapman-Enskog-Wilke-Lee
MUV	MUV01	MUV0BROK	General Pure Component Vapor Viscosity
KV	KV01	KV0STLTH	General Pure Component Vapor Thermal Conductivity

Liquid

Property Name	Route ID	Model Name	Description
PHILMX	PHILMXPA	ESPSAFT	Copolymer PCSAFT
HLMX	HLMXPA	ESPSAFT	Copolymer PCSAFT
GLMX	GLMXPA	ESPSAFT	Copolymer PCSAFT
SLMX	SLMXPA	ESPSAFT	Copolymer PCSAFT
VLMX	VLMXPA	ESPSAFT	Copolymer PCSAFT
MULMX	MULMX13	MUPOLY, MULMH	Aspen, Modified Mark-Houwink/van Krevelen, Andrade

Liquid			
Property Name	**Route ID**	**Model Name**	**Description**
KLMX	KLMXVKTR	KLMXVKTR	Vredeveld mixing, Modified van Krevelen, TRAPP
DLMX	DLMX02	DL1WCA	Wilke-Chang-Andrade
SIGLMX	SIGLMX01	SIG2HSS	General Pure Component Liquid Surface Tension, Power Law Mixing
PHIL	PHILPA	ESPSAFT0	Copolymer PCSAFT
HL	HLPA	ESPSAFT0	Copolymer PCSAFT
GL	GLPA	ESPSAFT0	Copolymer PCSAFT
SL	SLPA	ESPSAFT0	Copolymer PCSAFT
VL	VLPA	ESPSAFT0	Copolymer PCSAFT
DL	DL01	DL0WCA	Wilke-Chang-Andrade
MUL	MULMH	MUL0MH	Modified Mark-Houwink/van Krevelen, Andrade
KL	KL0VKTR	KL0VKTR	Modified van Krevelen, TRAPP

Solid			
Property Name	**Route ID**	**Model Name**	**Description**
HSMX	HSMXDVK	HS0DVK	Ideal mixing, van Krevelen
GSMX	GSMXDVK	GS0DVK	Ideal mixing, van Krevelen
SSMX	SSMXDVK	HS0DVK, GS0DVK	Ideal mixing, van Krevelen
VSMX	VSMXDVK	VS0DVK, VS0POLY	van Krevelen, Polynomial
HS	HSDVK	HS0DVK	van Krevelen
GS	GSDVK	GS0DVK	van Krevelen
SS	SSDVK	HS0DVK, GS0DVK	van Krevelen
VS	VSDVK	VS0DVK, VS0POLY	van Krevelen, Polynomial

Option Codes for PC-SAFT

The copolymer PC-SAFT has three option codes.

Option code 1. The user can use this option code to specify the copolymer type. The default type is the random copolymer (0). Other types are the alternative copolymer (1) and the block copolymer (2). All other values are assigned to the random copolymer.

Option code 2. This option code is restricted to the Sadowski's copolymer model in which a copolymer must be built only by two different types of segments (Gross and Sadowski, 2003; Becker et al., 2004). In order to use the Sadowski's copolymer model, this option code must be set to one.

Option code 3. The user can use this option code to turn off the association term from the copolymer PC-SAFT model by setting a non-zero value.

Sample Calculation Results for Copolymer PC-SAFT

In Figure 1, Aspen Plus applies the PC-SAFT EOS model to calculate both vapor-liquid and liquid-liquid equilibria for methanol-cyclohexane mixtures at p = 1.013 bar. This mixture exhibits an azeotropic vapor-liquid equilibrium at higher temperatures and shows a liquid-liquid equilibrium at lower temperatures. Both pure and binary parameters used are taken directly from the paper by Gross and Sadowski (2002b). The results show that the PC-SAFT model with the association term included can correlate phase equilibrium data well for associating mixtures.

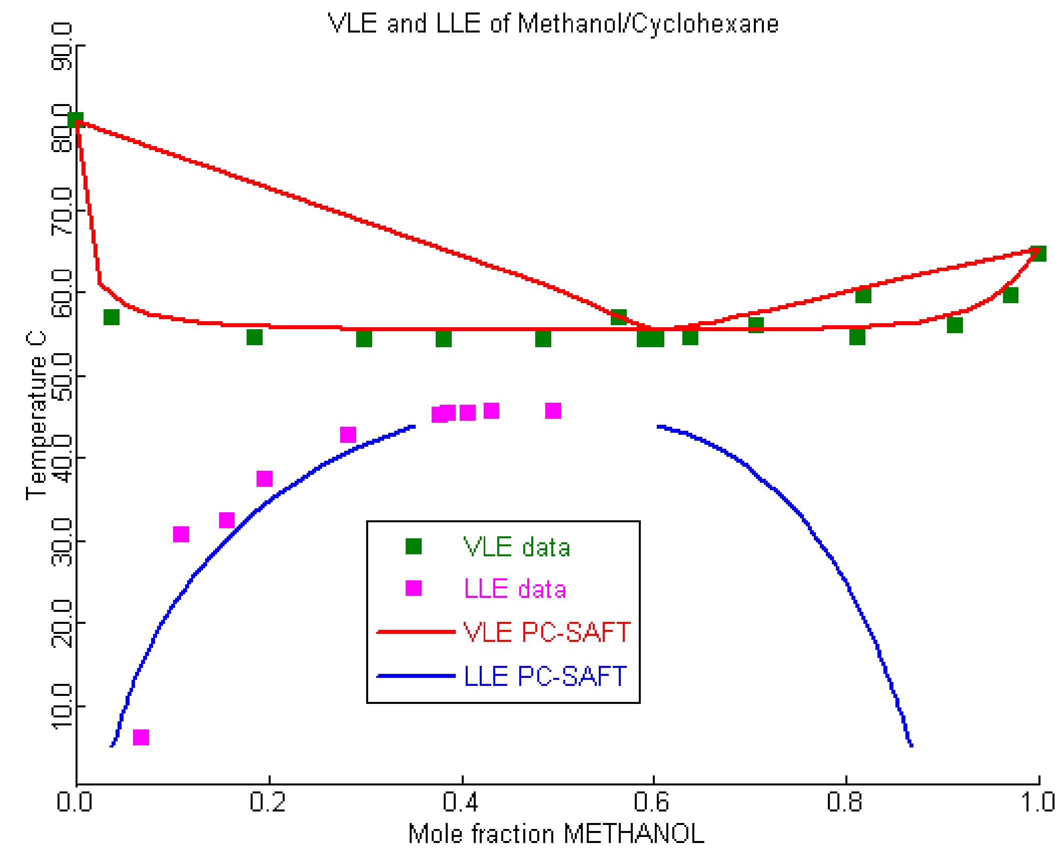

Figure 1. Isobaric vapor-liquid and liquid-liquid equilibria of methanol-cyclohexane at = 1.013 bar. Experimental data are taken from Jones and Amstell (1930) and Marinichev and Susarev (1965).

Figure 2 shows a model calculation for HDPE-Hexane mixtures. This system exhibits both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) at *p* = 50 bar. The pure parameters are taken directly from papers Gross and Sadowski (2001; 2002a). The binary parameter between hexane and ethylene segment is set to 0.012. The phase equilibrium calculations are carried by Flash3 block with Gibbs flash algorithm in Aspen Plus.

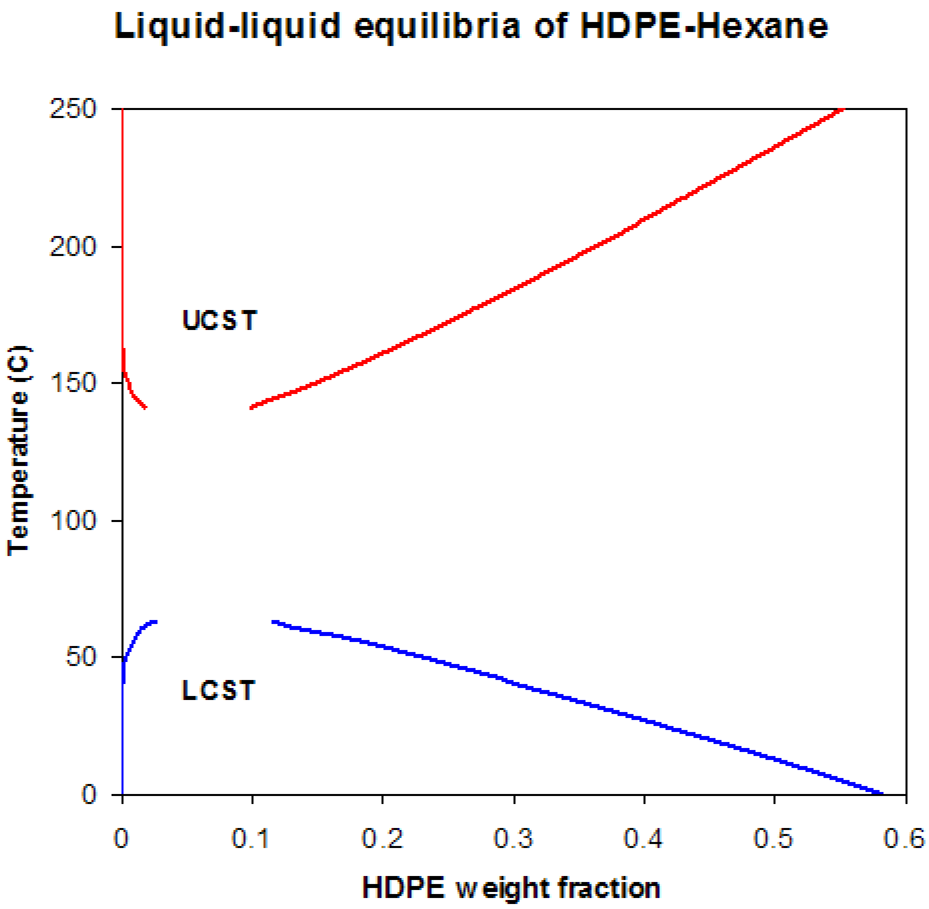

Figure 2. Liquid-liquid equilibria of HDPE-Hexane mixtures in a weight fraction-pressure plot by PC-SAFT EOS model. It shows both lower critical solution temperature (LCST) and upper critical solution temperature (UCST).

Figure 3 shows the vapor-liquid equilibrium of the mixture water-acetone at p = 1.703 bar. The dashed line represents PC-SAFT calculations where water is treated as an associating component and acetone as a polar component; the cross association in the mixture is not considered (κ_{ij} = -0.15). The solid line represents PC-SAFT calculations where the cross association between water and acetone is accounted for (κ_{ij} = -0.055) using a simple approach by Sadowski & Chapman et al. (2006). In this approach, the association energy and effective volume parameters of the non-associating component (acetone) are set to zero and to the value of the associating component (water), respectively. Further, the polar component is represented by the three pure-component parameters without using the dipolar model.

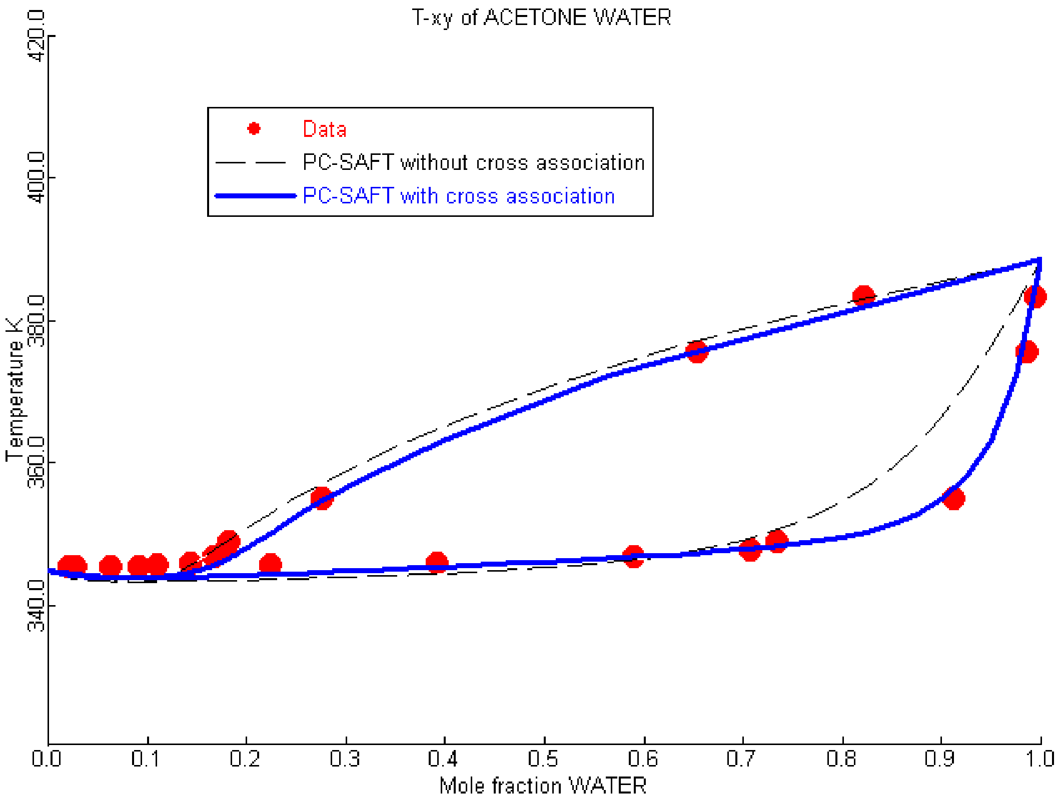

Figure 3. Vapor-liquid equilibrium of the mixture water-acetone at p = 1.703 bar. Experimental data are taken from Othmer and Morley (1946).

Figure 4 shows the liquid-liquid equilibria of polypropylene (PP)-n-pentane at three temperatures in a pressure-weight fraction plot. The weight average molecular weight of PP is M_w = 50.4 kg/mol, M_w/M_n = 2.2. Both pure and binary parameters used are taken directly from the paper by Gross and Sadowski (2002a).

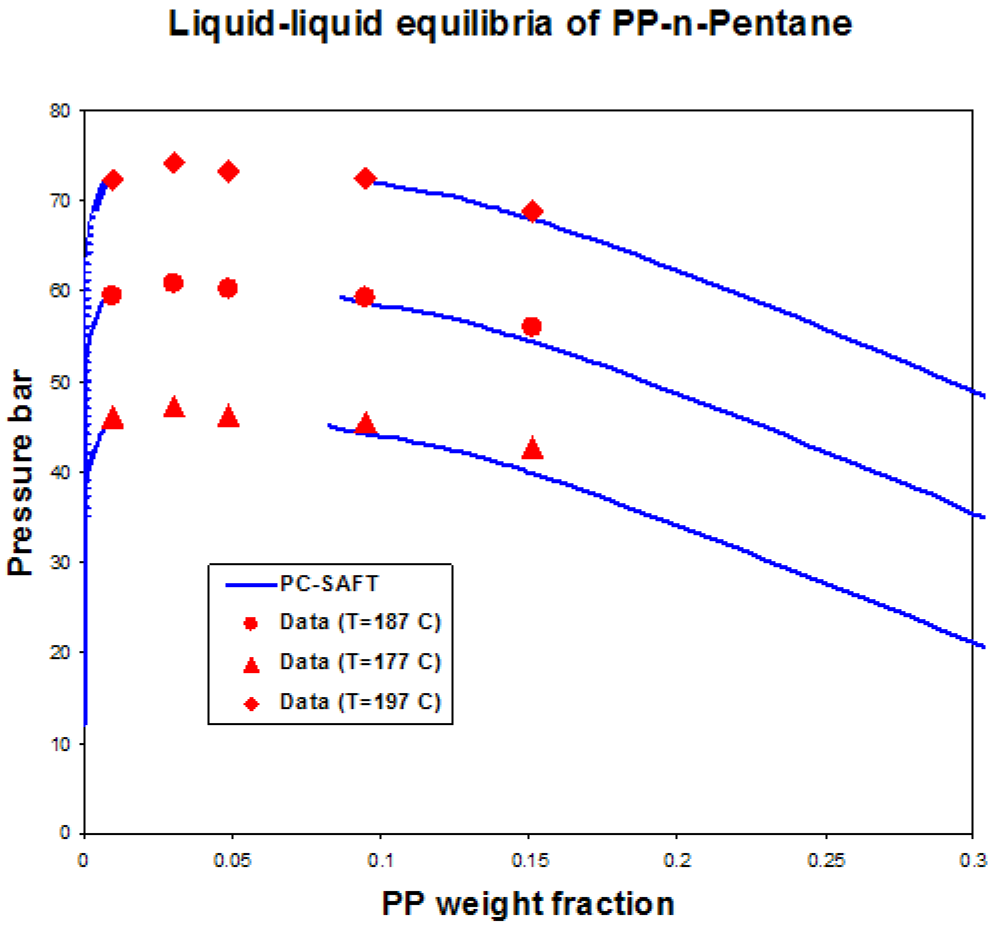

Figure 4. Liquid-liquid equilibria of PP-n-Pentane at three different temperatures. Comparison of experimental cloud points (Martin et al., 1999) to PC-SAFT calculations (κ_{ij} = 0.0137). The polymer was assumed to be monodisperse at M_w = 50.4 kg/mol.

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PPR78

The PPR78 method is based on the Predictive Peng-Robinson equation of state. It combines the model proposed by Peng and Robinson in 1978 with classical Van der Waals mixing rules involving a temperature-dependent binary interaction parameter $k_{ij}(T)$. These k_{ij} coefficients are predicted by PPR78 from the chemical structures of molecules within the mixture.

The minimum parameter requirements of the PPR78 property method are given in the tables labeled Parameters Required for the PPR78 Property Method (below) and Parameters Required for Common Flexible and Predictive Models. For details about optional parameters, and calculation of pure component and mixture properties, see *Physical Property Models*.

Mixture Types

The PPR78 method can represent the phase behavior of any fluid containing alkanes, alkenes, aromatic compounds, cycloalkanes, permanent gases (CO_2, N_2, H_2S, H_2), mercaptans, and water.

Ranges

You can expect reasonable results at all temperatures and pressures. The PPR78 property method is consistent in the critical region. Therefore, it does not exhibit anomalous behavior, unlike the activity coefficient property methods. Results are least accurate in the region near the mixture critical point.

Parameters Required for the PPR78 Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture Fugacity coefficient, Density	Predictive Peng-Robinson,	P78TC, P78PC, P78OMG, P78C (P78GRP or structure) and P78GBP, or P78KIJ
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Predictive Peng-Robinson,	P78TC, P78PC, P78OMG, P78C (P78GRP or structure) and P78GBP, or P78KIJ

PRMHV2

The PRMHV2 property method is based on the Peng-Robinson-MHV2 equation-of-state model, which is an extension of the Peng-Robinson equation of state. The UNIFAC model is used by default to calculate excess Gibbs energy in the MHV2 mixing rules. Other modified UNIFAC models and activity coefficient models can be used for excess Gibbs energy.

Besides the acentric factor, up to three polar parameters can be used to fit more accurately the vapor pressure of polar compounds.

The MHV2 mixing rules predict the binary interactions at any pressure. Using the UNIFAC model, the MHV2 mixing rules are predictive for any interaction that can be predicted by the UNIFAC model at low pressure.

The minimum parameter requirements of the PRMHV2 property method are given in the tables labeled Parameters Required for the PRMHV2 Property Method (below) and Parameters Required for Common Flexible and Predictive Models. For details about optional parameters, and calculation of pure component and mixture properties, see *Physical Property Models*.

Mixture Types

You can use the PRMHV2 property method for mixtures of non-polar and polar compounds. For light gases UNIFAC does not provide any interaction.

Range

You can use the PRMHV2 property method up to high temperatures and pressures. You can expect accurate predictions (4% in pressure and 2% in mole fraction at given temperature) up to about 150 bar. You can expect reasonable results at any condition, provided the UNIFAC interaction parameters are available. Results are least accurate close to the critical point.

Parameters Required for the PRMHV2 Property Method

Thermodynamic Properties	**Models**	**Parameter Requirements**
Vapor and liquid mixture Fugacity coefficient, Density	Peng-Robinson-MHV2,	TC, PC, OMEGA
	UNIFAC	UFGRP, GMUFQ, GMUFR
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Peng-Robinson-MHV2	TC, PC, OMEGA
	UNIFAC	UFGRP, GMUFQ, GMUFR

PRWS

The PRWS property method is based on the Peng-Robinson-Wong-Sandler equation-of-state model, which is based on an extension of the Peng-Robinson equation of state. The UNIFAC model is used to calculate excess Helmholtz energy for the mixing rules.

Besides the acentric factor, you can use up to three polar parameters to fit more accurately the vapor pressure of polar compounds. The Wong-Sandler mixing rules predict the binary interactions at any pressure. Using the UNIFAC model the PRWS property method is predictive for any interaction that can be predicted by UNIFAC at low pressure.

The minimum parameter requirements of the property method are given in the tables labeled Parameters Required for the PRWS Property Method (below) and Parameters Required for Common Flexible and Predictive Models. For details about the optional parameters, and about calculation of pure component and mixture properties, see *Physical Property Models*.

Mixture Types

You can use the PRWS property method for mixtures of non-polar and polar compounds, in combination with light gases.

Range

You can use the PRWS property method up to high temperatures and pressures. You can expect accurate predictions (3% in pressure and 2% in mole fraction at a given temperature) up to about 150 bar. You can expect reasonable results at any condition, provided UNIFAC interaction parameters are available. Results are least accurate close to the critical point.

Parameters Required for the PRWS Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture Fugacity coefficient, Density	Peng-Robinson-WS	TC, PC, OMEGA
	UNIFAC	UFGRP, GMUFR, GMUFQ
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP)
	Peng-Robinson-WS	TC, PC, OMEGA
	UNIFAC	UFGRP, GMUFR, GMUFQ

PSRK

The PSRK property method is based on the Predictive Soave-Redlich-Kwong equation-of-state model, which is an extension of the Redlich-Kwong-Soave equation of state.

Besides the acentric factor, you can use up to three polar parameters to fit more accurately the vapor pressure of polar compounds. The Holderbaum-Gmehling mixing rules or PSRK method predict the binary interactions at any pressure. Using UNIFAC the PSRK method is predictive for any interaction that can be predicted by UNIFAC at low pressure. The UNIFAC interaction parameter table has been extended for gases, for the PSRK method.

The minimum parameter requirements of the PSRK property method are given in the tables labeled Parameters Required for the PSRK Property Method (see below) and Parameters Required for Flexible and Predictive Models. For details about the optional parameters, and about calculation of pure component and mixture properties, see *Physical Property Models*.

Mixture Types

You can use the PSRK property method for mixtures of non-polar and polar compounds, in combination with light gases.

Range

You can use the PSRK property method up to high temperatures and pressures. You can expect accurate predictions at any conditions provided UNIFAC interaction parameters are available. Results are least accurate close to the critical point.

Parameters Required for the PSRK Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture Fugacity coefficient, Density	PSRK	TC, PC, OMEGA
	UNIFAC	UFGRP, GMUFR, GMUFQ
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	PSRK	TC, PC, OMEGA,
	UNIFAC	UFGRP, GMUFR, GMUFQ

RK-ASPEN

The RK-ASPEN property method is based on the Redlich-Kwong-Aspen equation-of-state model, which is an extension of Redlich-Kwong-Soave.

This property method is similar to RKS-BM, but it also applies to polar components such as alcohols and water. RK-ASPEN requires polar parameters that must be determined from regression of experimental vapor pressure data using DRS. Use the binary parameters to obtain best possible results for phase equilibria. RK-ASPEN allows temperature-dependent binary parameters. If the polar parameters are zero for all components and the binary parameters are constant, RK-ASPEN is identical to RKS-BM.

The minimum parameter requirements of the RK-ASPEN property method are given in the tables labeled Parameters Required for the RK-ASPEN Property Method (see below) and Parameters Required for Common Flexible and Predictive Models. For details about the optional parameters for this model, see *Physical Property Models*.

Mixture Types

You can use the RK-ASPEN property method for mixtures of non-polar and slightly polar compounds, in combination with light gases. It is especially suited for combinations of small and large molecules, such as nitrogen with n-Decane, or hydrogen-rich systems.

Range

You can use the RK-ASPEN property method up to high temperatures and pressures. You can expect reasonable results at any condition, but results are least accurate close to the critical point.

Parameters Required for the RK-ASPEN Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture Fugacity coefficient, Density	Redlich-Kwong-Aspen	TCRKA, PCRKA, OMEGARKA UFGRP, GMUFR, GMUFQ
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Redlich-Kwong-Aspen	TCRKA, PCRKA, OMEGARKA

RKSMHV2

The RKSMHV2 property method is based on the Redlich-Kwong-Soave MHV2 equation-of-state model, which is an extension of the Redlich-Kwong-Soave equation of state. The Lyngby modified UNIFAC model is used to calculate excess Gibbs energy for the MHV2 mixing rules.

Besides the acentric factor, you can use up to three polar parameters to fit more accurately the vapor pressure of polar compounds. The MHV2 mixing rules predict the binary interactions at any pressure. Using the Lyngby modified UNIFAC model, the Redlich-Kwong-Soave MHV2 model is predictive for any interaction that can be predicted by Lyngby modified UNIFAC at low pressure. The Lyngby modified UNIFAC interaction parameter table has been extended for gases for the MHV2 method.

The minimum parameter requirements of the RKSMHV2 property method are given in the tables labeled Parameters Required for the RKSMHV2 Property Method (see below) and Parameters Required for Common Flexible and Predictive Models. For details about optional parameters and calculation of pure component and mixture properties, see *Physical Property Models*.

Mixture Types

You can use the RKSMHV2 property method for mixtures of non-polar and polar compounds, in combination with light gases.

Range

You can use the RKSMHV2 property method up to high temperatures and pressures. You can expect accurate predictions (4% in pressure and 2% in mole fraction at given temperature) up to about 150 bar. You can expect reasonable results at any condition, provided Lyngby modified UNIFAC interactions are available. Results are least accurate close to the critical point.

Parameters Required for the RKSMHV2 Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture Fugacity coefficient, Density	Redlich-Kwong-Soave-MHV2	TC, PC, OMEGA
	Lyngby modified UNIFAC	UFGRPL, GMUFLR, GMUFLQ
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Redlich-Kwong-Soave-MHV2	TC, PC, OMEGA
	Lyngby modified UNIFAC	UFGRPL, GMUFLR, GMUFLQ

RKSWS

The RKSWS property method is based on the Redlich-Kwong-Soave-Wong-Sandler equation-of-state model, which is an extension of the Redlich-Kwong-Soave equation of state. The UNIFAC model is used to calculate excess Helmholtz energy for the mixing rules.

Besides the acentric factor,you can use up to three polar parameters to fit more accurately the vapor pressure of polar compounds. The Wong-Sandler mixing rules predict the binary interactions at any pressure. Using the UNIFAC model it is predictive for any interaction that can be predicted by UNIFAC at low pressure.

The minimum parameter requirements of the RKSWS property method are given in the tables labeled Parameters Required for the RKSWS Property Method (see below) and Parameters Required for Common Flexible and Predictive Models. For details about optional parameters and calculation of pure component and mixture properties, see *Physical Property Models*.

Mixture Types

You can use the RKSWS property method for mixtures of non-polar and polar compounds, in combination with light gases.

Range

You can use the RKSWS property method up to high temperatures and pressures. You can expect accurate predictions (3% in pressure and 2% in mole fraction at a given temperature) up to about 150 bar. You can expect reasonable results at any condition, provided UNIFAC interaction parameters are available. But results are least accurate close to the critical point.

Parameters Required for the RKSWS Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture Fugacity coefficient, Density	Redlich-Kwong-Soave-WS	TC, PC, OMEGA
	UNIFAC	UFGRP, GMUFR, GMUFQ
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Redlich-Kwong-Soave-WS	TC, PC, OMEGA
	UNIFAC	UFGRP, GMUFR, GMUFQ

SR-POLAR

The SR-POLAR property method is based on an equation-of-state model by Schwarzentruber and Renon, which is an extension of the Redlich-Kwong-Soave equation of state. You can apply the SR-POLAR method to both non-polar and highly polar components, and to highly nonideal mixtures. This method is recommended for high temperature and pressure applications

SR-POLAR requires:

- Polar parameters for polar components. These parameters are determined automatically using vapor pressure data generated from the General Pure Component Liquid Vapor Pressure model.
- Binary parameters to accurately represent phase equilibria. The binary parameters are temperature-dependent.

If you do not enter binary parameters, the Aspen Physical Property System estimates them automatically using VLE data generated from the UNIFAC group contribution method. Therefore, the SR-POLAR property method is predictive for any interaction that UNIFAC can predict at low pressures. The accuracy of the prediction decreases with increasing pressure. You cannot use UNIFAC to predict interactions with light gases.

SR-POLAR is an alternative property method that you can use for nonideal systems, instead of using an activity coefficient property method, such as WILSON.

Parameter requirements for the SR-POLAR property method are in the tables labeled Parameters Required for the SR-POLAR Property Method (see below) and Parameters Required for Common Flexible and Predictive Models. For details about optional parameters, and calculation of pure component and mixture properties, see *Physical Property Models*.

Mixture Types

You can use the SR-POLAR property method for mixtures of non-polar and polar compounds, in combination with light gases.

Range

You can use the SR-POLAR property method up to high temperatures and pressures. You can expect fair predictions up to about 50 bar. You can expect reasonable results at any condition, provided UNIFAC interaction parameters are available. But results are least accurate close to the critical point.

Parameters Required for the SR-POLAR Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture Fugacity coefficient, Density	Schwartzentruber-Renon	TC, PC, OMEGA, Optional: RKUPPn, RKUCn, RKUKAn, RKULAn, RKUKBn n = 0, 1, 2
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	(CPIG or CPIGDP)
	Schwartzentruber-Renon	Optional: RKUPPn, RKUCn, RKUKAn, RKULAn, RKUKBn n = 0, 1, 2

Common Models for Flexible and Predictive Equation-of-State Property Methods

The following table describes the models common to flexible and predictive property methods and their parameter requirements.

Parameters Required for Common Flexible and Predictive Models

General

Property/Purpose	Parameter Requirements
Mass balance, Conversion Mass-basis↔ Mole-basis	MW
Conversion Stdvol-basis↔ Mole-basis	VLSTD
Initialization of Flash calculations	PLXANT
Using Free-water option: solubility of water in organic phase	WATSOL
Enthalpy, enthalpy of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Transport Properties

Property	Models	Parameter Requirements
Vapor mixture Viscosity	Chung-Lee-Starling	TC, PC, OMEGA
Thermal Conductivity	Chung-Lee-Starling	TC, PC, OMEGA
Diffusivity	Dawson-Khoury-Kobayashi	MW, MUP, (STKPAR or LJPAR), VC
Surface tension	General Pure Component Liquid Surface Tension	(TC, PC, OMEGA) or SIGDIP
Liquid mixture Viscosity	Chung-Lee-Starling	TC, PC, OMEGA
Thermal Conductivity	Chung-Lee-Starling	TC, PC, OMEGA
Diffusivity	Wilke-Chang	MW, VB

Liquid Activity Coefficient Property Methods

The table labeled Liquid Activity Coefficient Property Methods (see Equations of State) lists property methods for nonideal and strongly nonideal mixtures at low pressures (maximum 10 atm). You can model permanent gases in liquid solution using Henry's law. Binary parameters for many component pairs are available in the Aspen Physical Property System databanks. The UNIFAC based property methods are predictive.

These property methods are not suited for electrolytes. In that case use an electrolyte activity coefficient property method. Model polar mixtures at high pressures with flexible and predictive equations of state. Non-polar mixtures are more conveniently modeled with equations-of-state. Petroleum mixtures are more accurately modeled with liquid fugacity correlations and equations of state.

In labeled Liquid Activity Coefficient Property Methods (see Equations of State) there are five different activity coefficient models and six different equation-of-state models. Each activity coefficient model is paired with a number of equation-of-state models to form 26 property methods. The description of the property methods are therefore divided into two parts:

- Equation of state
- Activity coefficient model

Each part discusses the characteristics of the specific model and its parameter requirements. Parameters of the models occurring in all property methods are given in the table labeled Parameters Required for Common Models.

Equations of State

This section discusses the characteristics and parameter requirements of the following equations of state:

- Ideal gas law
- Redlich-Kwong
- Nothnagel
- Hayden-O'Connell
- HF equation of state
- VPA/IK-CAPE Equation of State

Liquid Activity Coefficient Property Methods

Property Method	Gamma Model Name	Vapor Phase EOS Name
NRTL	NRTL	Ideal gas law
NRTL-2	NRTL	Ideal gas law
NRTL-RK	NRTL	Redlich-Kwong
NRTL-HOC	NRTL	Hayden-O'Connell
NRTL-NTH	NRTL	Nothnagel
UNIFAC	UNIFAC	Redlich-Kwong
UNIF-LL	UNIFAC	Redlich-Kwong
UNIF-HOC	UNIFAC	Hayden-O'Connell
UNIF-DMD	Dortmund modified UNIFAC	Redlich-Kwong-Soave
UNIF-LBY	Lyngby modified UNIFAC	Ideal Gas law
UNIQUAC	UNIQUAC	Ideal gas law
UNIQ-2	UNIQUAC	Ideal gas law
UNIQ-RK	UNIQUAC	Redlich-Kwong
UNIQ-HOC	UNIQUAC	Hayden-O'Connell
UNIQ-NTH	UNIQUAC	Nothnagel
VANLAAR	Van Laar	Ideal gas law
VANL-2	Van Laar	Ideal gas law
VANL-RK	Van Laar	Redlich-Kwong
VANL-HOC	Van Laar	Hayden-O'Connell
VANL-NTH	Van Laar	Nothnagel
WILSON	Wilson	Ideal gas law
WILS-2	Wilson	Ideal gas law
WILS-GLR	Wilson	Ideal gas law
WILS-LR	Wilson	Ideal gas law
WILS-RK	Wilson	Redlich-Kwong
WILS-HOC	Wilson	Hayden-O'Connell
WILS-NTH	Wilson	Nothnagel
WILS-HF	Wilson	HF equation of state

Property	Common Models
Vapor pressure	General Pure Component Liquid Vapor Pressure
Liquid molar volume	Rackett
Heat of vaporization	General Pure Component Heat of Vaporization
Vapor viscosity	General Pure Component Vapor Viscosity
Vapor thermal conductivity	General Pure Component Vapor Thermal Conductivity
Vapor diffusivity	Dawson-Khoury-Kobayashi
Surface tension	General Pure Component Liquid Surface Tension
Liquid viscosity	General Pure Component Liquid Viscosity
Liquid thermal conductivity	General Pure Component Liquid Thermal Conductivity
Liquid diffusivity	Wilke-Chang

Ideal Gas Law

The property methods that use the ideal gas law as the vapor phase model are:

- NRTL
- NRTL-2
- UNIF-LBY
- UNIQUAC
- UNIQ-2
- VANLAAR
- VANL-2
- WILSON
- WILS-2
- WILS-GLR
- WILS-LR

The ideal gas law is the simplest equation of state. It is also known as the combined laws of Boyle and Gay-Lussac.

Mixture Types

The ideal gas law cannot model association behavior in the vapor phase, as occurs with carboxylic acids. Choose Hayden-O'Connell or Nothnagel to model this behavior.

Range

The ideal gas law is valid for low pressures. It is not suited for modeling pressures exceeding several atm. For medium pressures, choose a Redlich-Kwong-based property method.

There are no component-specific parameters associated with the ideal gas law.

Redlich-Kwong

The property methods that use the Redlich-Kwong equation of state as the vapor phase model are:

- NRTL-RK
- UNIFAC
- UNIF-LL
- UNIQ-RK
- VANL-RK
- WILS-RK

The Redlich-Kwong equation of state is a simple cubic equation of state.

Mixture Types

The Redlich-Kwong equation of state cannot model association behavior in the vapor phase, as occurs with carboxylic acids.

Range

The Redlich-Kwong equation of state describes vapor phase properties accurately up to medium pressures.

The parameter requirements for the Redlich-Kwong equation of state are given in the following table. For details about the model, see *Physical Property Models*.

Parameters Required for Redlich-Kwong Property Methods

Thermodynamic Properties	**Models**	**Parameter Requirements**
Vapor mixture Fugacity coefficient, Density	Redlich-Kwong	TC, PC
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Redlich-Kwong	TC, PC

Nothnagel

The property methods that use the Nothnagel equation of state as vapor phase model are:

- NRTL-NTH
- UNIQ-NTH
- VANL-NTH
- WILS-NTH

The Nothnagel equation of state accounts for dimerization in the vapor phase at low pressure. Dimerization affects VLE; vapor phase properties, such as enthalpy and density; and liquid phase properties, such as enthalpy.

Mixture Types

The Nothnagel equation of state can model dimerization in the vapor phase, as occurs with mixtures containing carboxylic acids.

Range

Do not use the Nothnagel based property methods at pressures exceeding several atm. For vapor phase association up to medium pressure choose the Hayden-O'Connell equation.

Parameter requirements for the Nothnagel equation of state are given in the following table. Enter equilibrium constants of association directly (NTHK). Or calculate them from the pure component parameters NTHA, elements 1 to 3 (b_i, p_i and d_i). If parameters are not available, the Aspen Physical Property System uses default values. For prediction, the Hayden-O'Connell correlation is more accurate. For details about the models, see *Physical Property Models*.

Parameters Required for Nothnagel Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Nothnagel	TB, TC, PC and (NTHA or NTHK)
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Nothnagel	TB, TC, PC and (NTHA or NTHK)

Hayden-O'Connell

The property methods that use the Hayden-O'Connell equation of state as vapor phase model are:

- NRTL-HOC
- UNIF-HOC
- UNIQ-HOC
- VANL-HOC
- WILS-HOC

The Hayden-O'Connell equation of state predicts solvation and dimerization in the vapor phase, up to medium pressure. Dimerization affects VLE; vapor phase properties, such as enthalpy and density; and liquid phase properties, such as enthalpy.

Mixture Types

The Hayden-O'Connell equation reliably predicts solvation of polar compounds and dimerization in the vapor phase, as occurs with mixtures containing carboxylic acids.

Range

Do not use the Hayden-O'Connell-based property methods at pressures exceeding 10 to 15 atm.

Parameter requirements for the Hayden-O'Connell equation of state are given in the following table. For details about the model, see *Physical Property Models*.

Parameters Required for Hayden-O'Connell Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Hayden-O'Connell	TC, PC, RGYR, MUP, HOCETA
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	Hayden-O'Connell	TC, PC, RGYR, MUP, HOCETA

HF Equation of State

The only property methods that use the HF equation of state as the vapor phase model are WILS-HF and ENRTL-HF.

For HF-hydrocarbon mixtures, the Wilson activity coefficient model is usually best suited for preventing nonrealistic liquid phase splitting.

The HF equation of state predicts the strong association of HF the vapor phase at low pressures. Association (mainly hexamerization) affects VLE, vapor phase properties, such as enthalpy and density, and liquid phase properties, such as enthalpy.

Mixture Types

The HF equation of state reliably predicts the strong association effects of HF in a mixture.

Range

Do not use the WILS-HF property method at pressures exceeding 3 atm.

Parameters for the HF equation of state are built-in for temperatures up to 373 K. You can enter parameters and regress them using the Aspen Physical Property System Data Regression System (DRS), if necessary . For details about the model, see *Physical Property Models*.

VPA/IK-CAPE Equation of State

The VPA/IK-CAPE equation of state is similar to the HF equation of state but allows dimerization and tetramerization. No property method uses this equation of state by default. It is recommended that this equation of state is used in place of the HF equation of state with the WILS-HF and ENRTL-HF property methods, when dimerization and tetramerization is expected.

The main assumption of the model is that only molecular association causes the gas phase nonideality. Attractive forces between the molecules and the complexes are neglected.

There are three kinds of associations which can be modeled:

- Dimerization (examples: formic acid, acetic acid)
- Tetramerization (example: acetic acid)
- Hexamerization (example: hydrogen fluoride)

Mixture Types

The VPA/IK-CAPE equation of state can be used to model strong association effects such as the presence of dimers, tetramers and hexamers. Use the VPA model for associating compounds like acids and hydrogen fluoride.

Range

Do not use the VPA/IK-CAPE equation of state at pressures exceeding 3 atmospheres. Parameters (equilibrium constants) for the formation of dimers, tetramers and hexamers are not built in to the Aspen Physical Property System.

You can enter parameters and regress them using the Aspen Physical Property Data Regression System (DRS)

Activity Coefficient Models

This section discusses the characteristics and parameter requirements of the following activity coefficient models:

- NRTL
- UNIFAC
- UNIQUAC
- Van Laar
- Wilson

NRTL

The property methods that use the NRTL activity coefficient model are listed in the following table:

NRTL Property Methods

		Binary Parameters				
Property Method Name	**Dataset Number**	**VLE † Lit Reg**	**LLE † Lit Reg**	**Henry † Lit Reg**	**Vapor Phase EOS Name**	**Poynting Correction**
NRTL	1	X X	— X	X X	Ideal Gas law	—
NRTL-2	2	X X	— X	X X	Ideal Gas law	—
NRTL-RK	1	— X	— —	X X	Redlich-Kwong	X
NRTL-HOC	1	— X	— —	X X	Hayden-O'Connell	X
NRTL-NTH	1	— —	— —	X X	Nothnagel	X

†An X in the Lit columns indicates the parameters were obtained from the literature. An X in the Reg columns indicates the parameters were regressed by AspenTech from experimental data in the Dortmund Databank (DDB).

The NRTL model can describe VLE and LLE of strongly nonideal solutions. The model requires binary parameters. Many binary parameters for VLE and LLE, from literature and from regression of experimental data, are included in the Aspen Physical Property System databanks. For details, see Binary Parameter Databanks in Physical Property Data in the help.

You can model the solubility of supercritical gases using Henry's law. Henry coefficients are available in the Aspen Physical Property System databanks for many solutes with water and other solvents. For details, see Binary Parameter Databanks in Physical Property Data in the help.

The property methods with a vapor phase model that can be used up to moderate pressures, have the Poynting correction included in the liquid fugacity coefficient calculation. See the table labeled NRTL Property Methods (above) .

Heat of mixing is calculated using the NRTL model.

You can use separate data sets for the NRTL binary parameters to model properties or equilibria at different conditions. It is also possible to use one data set for VLE and a second data set for LLE (use NRTL and NRTL-2) property methods are identical except for the data set number they use. For example, you can use these property methods in different flowsheet sections or column sections.

Mixture Types

The NRTL model can handle any combination of polar and non-polar compounds, up to very strong nonideality.

Range

Parameters should be fitted in the temperature, pressure, and composition range of operation. No component should be close to its critical temperature.

Parameter requirements for the NRTL activity coefficient model are given in the following table. For details about the model, see *Physical Property Models*.

Parameters Required for NRTL Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture Fugacity coefficient, Gibbs energy	NRTL liquid activity coefficient	NRTL
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Solute: (VC or VLBROC)

Thermodynamic Properties	Models	Parameter Requirements
Enthalpy, Entropy	General Pure Component Ideal Gas Heat Capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	DHVLWT or DHVLDP
	NRTL liquid activity coefficient	NRTL
Density	Rackett	TC, PC, (VC or VCRKT), (ZC or RKTZRA)

UNIFAC

UNIFAC is an activity coefficient model, like NRTL or UNIQUAC. But it is based on group contributions, rather than molecular contributions. With a limited number of group parameters and group-group interaction parameters, UNIFAC can predict activity coefficients. The following table lists the property methods based on UNIFAC.

UNIFAC Property Methods

Property Method Name	Model Name	Parameters Rev. Yr	Tmin /K	Tmax /K	Henry Lit Reg	Vapor Phase EOS Name	Poynting Correction
UNIFAC	UNIFAC	5, 1991	290	420	X X	Redlich-Kwong	X
UNIF-LL	UNIFAC	—, 1991	280	310	X X	Redlich-Kwong	X
UNIF-HOC	UNIFAC	5, 1991	290	420	X X	Hayden-O'Connell	X
UNIF-DMD	DMD-UNIF	1, 1993	290	420	X X	Redlich-Kwong-Soave	X
UNIF-LBY	LBY-UNIF	—, 1987	290	420	X X	Ideal Gas law	—

†An X in the Lit columns indicates the parameters were obtained from the literature. An X in the Reg columns indicates the parameters were regressed by AspenTech from experimental data in the Dortmund Databank (DDB).

The original version of UNIFAC can predict VLE and LLE, using two sets of parameters. So there are two property methods based on the original UNIFAC model, one using the VLE data set (UNIFAC), the other using the LLE data set (UNIF-LL).

There are two modifications to the UNIFAC model. They are named after the location of the universities where they were developed: Lyngby in Denmark, and Dortmund in Germany. The corresponding property methods are UNIF-LBY and UNIF-DMD. Both modifications:

- Include more temperature-dependent terms of the group-group interaction parameters
- Predict VLE and LLE with a single set of parameters
- Predict heats of mixing better

In the Dortmund modification, the prediction for activity coefficients at infinite dilution is improved.

You can model the solubility of supercritical gases using Henry's law. Henry coefficients are available in the Aspen Physical Property System databanks for many solutes with water and other solvents (see Henry's Law Constants in Physical Property Data).

The option sets with a vapor phase model that can be used up to moderate pressures, have the Poynting correction included in the liquid fugacity coefficient calculation (see the table labeled UNIFAC Property Methods above).

Heats of mixing are calculated using the UNIFAC or modified UNIFAC models.

Mixture Types

The UNIFAC and modified UNIFAC models can handle any combination of polar and nonpolar compounds. Dissolved gas in solutions can be handled with Henry's Law. However, gas-solvent interactions are not predicted by UNIFAC.

Range

No component should be close to its critical temperature. Approximate temperature ranges are indicated in the table labeled UNIFAC Property Methods (above).

The parameter sets for all UNIFAC models are regularly revised and extended. The table labeled UNIFAC Property Methods (above) gives the revision number currently used in the Aspen Physical Property System. For details on the parameters used, see Group Contribution Method Functional Groups in Physical Property Data.

The minimum parameter requirements for the UNIFAC and modified UNIFAC models are given in the following table. For details about the models, see *Physical Property Models*.

Parameters Required for the UNIFAC Property Methods

Thermodynamic Properties	Models		Parameter Requirements
Liquid mixture Fugacity coefficient, Gibbs energy	One of:	UNIFAC	UFGRP
		Dortmund modified UNIFAC	UFGRPD
		Lyngby modified UNIFAC	UFGRPL
	General Pure Component Liquid Vapor Pressure		PLXANT
	Henry's constant		Solvent: VC, Solute-solvent: HENRY
	Brelvi-O'Connell		Solvent: TC, PC, (ZC or RKTZRA), Solute: (VC or VLBROC)
Enthalpy, Entropy	General Pure Component Ideal Gas Heat Capacity		CPIG or CPIGDP
	General Pure Component Heat of Vaporization		TC, (DHVLWT or DHVLDP)
	One of:	UNIFAC	UFGRP
		Dortmund modified UNIFAC	UFGRPD
		Lyngby modified UNIFAC	UFGRPL
Density	Rackett		TC, PC, (VC or VCRKT), (ZC or RKTZRA)

UNIQUAC

The property methods that use the UNIQUAC activity coefficient model are listed in the following table.

UNIQUAC Property Methods

Property Method Name	Dataset Number	Binary Parameters VLE † Lit Reg	LLE † Lit Reg	Henry † Lit Reg	Vapor Phase EOS Name	Poynting Correction
UNIQUAC	1	X X	X X	X X	Ideal Gas law	—
UNIQ-2	2	X X	X X	X X	Ideal Gas law	—
UNIQ-RK	1	— X	— —	X X	Redlich-Kwong	X
UNIQ-HOC	1	— X	— —	X X	Hayden-O'Connell	X
UNIQ-NTH	1	— —	— —	X X	Nothnagel	X

†An X in the Lit columns indicates the parameters were obtained from the literature. An X in the Reg columns indicates the parameters were regressed by AspenTech from experimental data in the Dortmund Databank (DDB).

The UNIQUAC model can describe strongly nonideal liquid solutions and liquid-liquid equilibria. The model requires binary parameters. Many binary parameters for VLE and LLE, from literature and from regression of experimental data, are included in the Aspen Physical Property System databanks (for details, see Binary Parameters for Vapor-Liquid Applications in Physical Property Data in the help).

You can model the solubility of supercritical gases using Henry's law. Henry coefficients are available from the databank (see Henry's Law Constants in Physical Property Data in the help).

The property methods with a vapor phase model that can be used up to moderate pressures, have the Poynting correction included in the liquid fugacity coefficient calculation (see the table labeled UNIQUAC Property Methods above).

Heats of mixing are calculated using the UNIQUAC model.

You can use separate data sets for the UNIQUAC binary parameters to model properties or equilibria at different conditions. It is also possible to use one data set for VLE and a second data set for LLE (use UNIQUAC and UNIQ-2). The property methods are identical except for the data set number they use. For example, you can use these options sets in different flowsheet sections or column sections.

Mixture Types

The UNIQUAC model can handle any combination of polar and non-polar compounds, up to very strong nonideality.

Range

Parameters should be fitted in the temperature, pressure, and composition range of operation. No component should be close to its critical temperature.

Parameter requirements for the UNIQUAC activity coefficient model are given in the following table. For details about the model, see *Physical Property Models*.

Parameters Required for UNIQUAC Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture Fugacity coefficient, Gibbs energy	UNIQUAC liquid activity coefficient	GMUQR, GMUQQ, UNIQ
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Solute: (VC or VLBROC)
Enthalpy, Entropy	General Pure Component Ideal Gas Heat Capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	TC, (DHVLWT or DHVLDP)
	UNIQUAC liquid activity coefficient	GMUQR, GMUQQ, UNIQ
Density	Rackett	TC, PC, (VC or VCRKT), (ZC or RKTZRA)

Van Laar

The property methods that use the Van Laar activity coefficient model are listed in the following table.

Van Laar Property Methods

Property Method Name	Dataset number	Binary Parameters VLE † Lit Reg	LLE † Lit Reg	Henry † Lit Reg	Vapor Phase EOS Name	Poynting Correction
VANLAAR	1	— —	— —	X X	Ideal Gas law	—
VANL-2	2	— —	— —	X X	Ideal Gas law	—
VANL-RK	1	— —	— —	X X	Redlich-Kwong	X
VANL-HOC	1	— —	— —	X X	Hayden-O'Connell	X
VANL-NTH	1	— —	— —	X X	Nothnagel	X

†An X in the Lit columns indicates the parameters were obtained from the literature. An X in the Reg columns indicates the parameters were regressed by AspenTech from experimental data in the Dortmund Databank (DDB).

The Van Laar model can describe nonideal liquid solutions with positive deviations from Raoult's law (see Activity Coefficient Method in Overview of Aspen Physical Property Methods). The model requires binary parameters.

You can model the solubility of supercritical gases using Henry's law. Henry coefficients are available from the Aspen Physical Property System databank (see Henry's Law Constants in Physical Property Data in the help).

The property methods with a vapor phase model that can be used up to moderate pressures, have the Poynting correction included in the liquid fugacity coefficient calculation (see the table labeled Van Laar Property Methods above).

Heats of mixing are calculated using the Van Laar model.

You can use separate data sets to model properties or equilibria at different conditions (use VANLAAR and VANL-2). The property methods are identical except for the data set number they use. For example, you can use these property methods in different flowsheet or column sections.

Mixture Types

The Van Laar model can handle any combination of polar and non-polar compounds with positive deviations from Raoult's law.

Range

Parameters should be fitted in the temperature range of operation. No component should be close to its critical temperature.

Parameter requirements for the Van Laar activity coefficient model are given in the following table. For details about the model, see *Physical Property Models*.

Parameters Required for Van Laar Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture Fugacity coefficient, Gibbs energy	Van Laar liquid activity coefficient	VANL
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Solute: (VC or VLBROC)
Enthalpy, Entropy	General Pure Component Ideal Gas Heat Capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	TC, (DHVLWT or DHVLDP)
	Van Laar liquid activity coefficient	VANL
Density	Rackett	TC, PC, (VC or VCRKT), (ZC or RKTZRA)

Wilson

The property methods that use the Wilson activity coefficient model or the Wilson Model with Liquid Molar Volume are listed in the following table. Only WILS-VOL uses the latter model.

Wilson Property Methods

		Binary Parameters				
Property Method Name	Dataset number	VLE Lit Reg	LLE Lit Reg	Henry Lit Reg	Vapor Phase EOS Name	Poynting Correction
WILSON	1	X X	— —	X X	Ideal Gas law	—
WILS-2	2	X X	— —	X X	Ideal Gas law	—

		Binary Parameters				
Property Method Name	**Dataset number**	**VLE Lit Reg**	**LLE Lit Reg**	**Henry Lit Reg**	**Vapor Phase EOS Name**	**Poynting Correction**
WILS-GLR	1	X X	— —	X X	Ideal Gas law	—
WILS-LR	1	X X	— —	X X	Ideal Gas law	—
WILS-RK	1	— X	— —	X X	Redlich-Kwong	X
WILS-HOC	1	— X	— —	X X	Hayden-O'Connell	X
WILS-NTH	1	— —	— —	X X	Nothnagel	X
WILS-HF	1	— —	— —	X X	HF	X
WILS-VOL	1	— —	— —	X X	Redlich-Kwong	X

†An X in the Lit columns indicates the parameters were obtained from the literature. An X in the Reg columns indicates the parameters were regressed by AspenTech from experimental data in the Dortmund Databank (DDB).

The Wilson model can describe strongly nonideal liquid solutions. The model cannot handle two liquid phases. In that case, use NRTL or UNIQUAC. The model requires binary parameters. Many binary parameters for VLE, from literature and from regression of experimental data, are included in the Aspen Physical Property System databanks (for details, see Binary Parameters for Vapor Liquid Applications in Physical Property Data in the help).

The solubility of supercritical gases can be modeled using Henry's law. Henry coefficients are available from the databank for many solutes with water and other solvents (see Henry's Law Constants in Physical Property Data in the help).

The property methods with a vapor phase model that can be used up to moderate pressures, have the Poynting correction included in the liquid fugacity coefficient calculation (see the table labeled Wilson Property Methods above).

Heats of mixing are calculated using the Wilson model.

You can use separate data sets for the Wilson binary parameters to model properties or equilibria at different conditions (use WILSON and WILS-2). The property methods are identical except for the data set number they use. For example, you can use these property methods in different flowsheet or column sections.

Mixture Types

The Wilson model can handle any combination of polar and non-polar compounds, up to very strong nonideality.

Range

Parameters should be fitted in the temperature, pressure, and composition range of operation. No component should be close to its critical temperature.

Parameter requirements for the Wilson activity coefficient model are given in the table below. For details about the model, see *Physical Property Models*.

Parameters Required for the Wilson Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture Fugacity coefficient, Gibbs energy	Wilson liquid activity coefficient	WILSON
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Solute: (VC or VLBROC)
Enthalpy, Entropy	General Pure Component Ideal Gas Heat Capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	TC, (DHVLWT or DHVLDP)
	Wilson liquid activity coefficient	WILSON
Density	Rackett	TC, PC, (VC or VCRKT), (ZC or RKTZRA)

Common Models for Liquid Activity Coefficient Property Methods

The following table describes the models common to activity coefficient property methods and their parameter requirements.

Parameters Required For Common Models

General

Property/Purpose	Parameter Requirements
Mass balance, Conversion Mass-basis↔ Mole-basis	MW
Conversion Stdvol-basis↔ Mole-basis	VLSTD
Using Free-water option: solubility of water in organic phase	WATSOL
Enthalpy, enthalpy of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Transport Properties

Property	Models	Parameter Requirements
Vapor mixture Viscosity	General Pure Component Vapor Viscosity	MW; (MUP and (STKPAR or LJPAR) or MUVDIP
Thermal conductivity	General Pure Component Vapor Thermal Conductivity	MW or KVDIP
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	General Pure Component Liquid Surface Tension	(TC, PC, OMEGA) or SIGDIP
Liquid mixture Viscosity	General Pure Component Liquid Viscosity	MULAND or MULDIP
Thermal Conductivity	General Pure Component Liquid Thermal Conductivity	(MW, TC, TB) or KLDIP
Diffusivity	Wilke-Chang	MW, VB

Electrolyte Property Methods

The following table lists property methods for electrolyte solutions. Electrolyte solutions are extremely nonideal because of the presence of charged species. Property methods based on correlations can handle specific components under well-described conditions; rigorous models are generally applicable. The electrolyte-NRTL-based property methods ELECNRTL, ENRTL-RK, and ENRTL-SR can handle mixed solvent systems at any concentration. The PITZER property method is accurate for aqueous solutions up to 6M. Binary parameters for many component pairs are available in the databanks. B-PITZER is predictive but less accurate. You can use these property methods at low pressures (maximum 10 atm). ENRTL-HF is similar to ELECNRTL, but with a vapor phase model for the strong HF association. This property method should be used at low pressures (maximum 3 atm). Permanent gases in liquid solution can be modeled by using Henry's law. Transport properties are calculated by standard correlations with corrections for the presence of electrolytes.

Electrolyte Property Methods

Correlation-Based Property Methods

Property Method	Correlation	System
AMINES	Kent-Eisenberg	MEA, DEA, DIPA, DGA
APISOUR	API Sour water correlation	H2O, NH3, CO2, H2S
GPSWAT	GPSWAT sour water correlation	H2O, NH3, CO2, H2S + light gases

Activity Coefficient Model-Based Property Methods

Property Method	Gamma Model Name	Vapor Phase EOS Name
ELECNRTL	Electrolyte NRTL	Redlich-Kwong
ENRTL-HF	Electrolyte NRTL	HF equation of state
ENRTL-HG	Electrolyte NRTL	Redlich-Kwong
ENRTL-RK	Unsymmetric Electrolyte NRTL	Redlich-Kwong
ENRTL-SR	Symmetric Electrolyte NRTL	Redlich-Kwong
PITZER	Pitzer	Redlich-Kwong-Soave
PITZ-HG	Pitzer	Redlich-Kwong-Soave
B-PITZER	Bromley-Pitzer	Redlich-Kwong-Soave

Other Property Methods

Property Method
OLI

Common Models For Rigorous Property Methods

Property	Model
Vapor pressure	General Pure Component Liquid Vapor Pressure
Liquid molar volume	Rackett, Clarke
Heat of vaporization	General Pure Component Heat of Vaporization
Infinite dilution heat capacity	Criss-Cobble
Vapor viscosity	General Pure Component Vapor Viscosity
Vapor thermal conductivity	General Pure Component Vapor Thermal Conductivity
Vapor diffusivity	Dawson-Khoury-Kobayashi
Surface tension	General Pure Component Liquid Surface Tension, Onsager-Samaras
Liquid viscosity	General Pure Component Liquid Viscosity, Jones-Dole
Liquid thermal conductivity	General Pure Component Liquid Thermal Conductivity, Riedel
Liquid diffusivity	Wilke-Chang, Nernst-Hartley

Do not use the electrolyte property methods for nonelectrolyte systems. See Classification of Property Methods and Recommended Use for more help.

For general thermodynamic principles, see Electrolyte Models in Overview of Aspen Physical Property Methods. The Electrolyte Calculation section contains specifics on electrolyte calculation. For details on methods, see Property Calculation Methods and Routes. The property method descriptions give the minimum parameter requirements for the thermodynamic property models used, also of the common thermodynamic property models. The general and transport property parameter requirements for coefficient-based property methods are in the table labeled Parameters Required for General and Transport Models. For details on models, see *Physical Property Models*.

AMINES

The AMINES property method uses the Kent-Eisenberg method for K-values and enthalpy. It is designed for systems containing water, one of four ethanolamines, hydrogen sulfide, carbon dioxide, and other components typically present in gas-sweetening processes. It can be used for the following four amines:

- Monoethanolamine (MEA)
- Diethanolamine (DEA)
- Diisopropanolamine (DIPA)
- Diglycolamine (DGA)

Range

Use the AMINES property method for amine systems with ranges of:

	MEA	**DEA**	**DIPA**	**DGA**
Temperature (°F)	90 – 280	90 – 275	90 – 260	90 – 280
Maximum H2S or CO2 Loading (moles gas/mole amine)	0.5	0.8	0.75	0.5
Amine Concentration in Solution (mass percent)	5 – 40	10 – 50	10 – 50	30 – 75

If the amine concentration is outside the recommended range, the Chao-Seader method is used for K-values (only for that particular property evaluation).

Refer to the following table for parameter requirements for this property method.

Parameters Required for the AMINES Property Method

General

Property/Purpose	**Parameter Requirements**
Mass balance, Conversion Mass-basis↔ Mole-basis	MW
Conversion Stdvol-basis↔ Mole-basis	VLSTD
Using free-water option: solubility of water in organic phase	WATSOL
Enthalpy, enthalpy of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Thermodynamic Properties

Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient Density	Redlich-Kwong	TC; PC
Enthalpy, entropy	General pure component ideal gas heat capacity	CPIG or CPIGDP
Liquid mixture Fugacity coefficient. Gibbs energy	Scatchard-Hildebrand activity coefficient	TC; DELTA; VLCVT1; GMSHVL
	Chao-Seader pure component fugacity coefficient	TC; PC; OMEGA
	General pure component liquid vapor pressure (amines and water only)	PLXANT
	Kent-Eisenberg (H2S and CO2 only)	—
Enthalpy, entropy	General pure component heat of vaporization	TC; PC;DHVLWT or DHVLDP
Density	Rackett/Campbell-Thodos molar volume	TC; PC: VC or VCRKT; ZC or RKTZRA

Transport Properties

Properties	Models	Parameter Requirements
Vapor mixture Viscosity	Dean-Stiel	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP; TC, PC, VC
Thermal conductivity	General Pure Component Vapor Thermal Conductivity	MW, TC, PC, VC, ZC
Diffusivity	Dawson-Khoury-Kobayaski	MW; MUP and (STKPAR or LJPAR); VC
Surface tension	General Pure Component Liquid Surface Tension	(TC, PC, OMEGA) or SIGDIP
Liquid mixture Viscosity	General Pure Component Liquid Viscosity	MULAND or MULDIP
Thermal Conductivity	General Pure Component Liquid Thermal Conductivity	(MW, TC, TB) or KLDIP
Diffusivity	Wilke-Chang	MW, VB

APISOUR

The APISOUR property method:

- Uses the API procedure for K-values and enthalpy of sour water systems.
- Is designed for sour water systems containing primarily water, ammonia, hydrogen sulfide and carbon dioxide.
- Is applicable in the temperature range of 20 – 140°C.
- Has an overall average error between measured and predicted partial pressures of about 30% for ammonia, carbon dioxide, and hydrogen sulfide.
- Does not require any user-supplied parameters.
- Is recommended for fast calculation of sour water systems at limited concentration. For more accurate results, use the ELECNRTL property method.
- Does not depend on any CHEMISTRY input. Do not specify Chemistry ID in any Electrolyte calculation options field.

Note: APISOUR uses an activity coefficient method such as NRTL or Wilson to calculate fugacity coefficients for components other than water, ammonia, hydrogen sulfide, or carbon dioxide. To specify this method, on the **Methods | Selected Methods | APISOUR | Models** sheet, select a model for calculating gamma. The default is GMRENON which uses NRTL.

Parameter requirements for the APISOUR property method are listed in the following table.

Parameters Required for the APISOUR Property Method

General

Property/Purpose	**Parameter Requirements**
Mass balance, Conversion Mass-basis↔ Mole-basis	MW
Conversion Stdvol-basis↔ Mole-basis	VLSTD
Using Free-water option: solubility of water in organic phase	WATSOL
Enthalpy, enthalpy of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Transport Properties

Properties	Models	Parameter Requirements
Vapor mixture Viscosity	General Pure Component Vapor Viscosity	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal conductivity	General Pure Component Vapor Thermal Conductivity	MW or KVDIP
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	General Pure Component Liquid Surface Tension	(TC, PC, OMEGA) or SIGDIP
Liquid mixture Viscosity	General Pure Component Liquid Viscosity	MULAND or MULDIP
Thermal Conductivity	General Pure Component Liquid Thermal Conductivity	(MW, TC, TB) or KLDIP
Diffusivity	Wilke-Chang	MW, VB

ELECNRTL

The ELECNRTL property method is the most versatile electrolyte property method. It can handle very low and very high concentrations. It can handle aqueous and mixed solvent systems.

The ELECNRTL property method is fully consistent with the NRTL-RK property method: the molecular interactions are calculated exactly the same way, therefore ELECNRTL can use the databank for binary molecular interaction parameters for the NRTL-RK property method.

Many binary and pair parameters and chemical equilibrium constants from regression of experimental data are included in Aspen Physical Property System databanks. See Electrolytes Data in Physical Property Data in the help, for details on the systems included, the sources of the data, and the ranges of application.

The solubility of supercritical gases can be modeled using Henry's law. Henry coefficients are available from the databank (see Activity Coefficient Method in Overview of Aspen Physical Property Methods).

Heats of mixing are calculated using the electrolyte NRTL model.

The Redlich-Kwong equation of state is used for all vapor phase properties, which cannot model association behavior in the vapor phase as occurs with carboxylic acids or HF. For carboxylic acids, choose Hayden-O'Connell or Nothnagel; for HF choose ENRTL-HF.

Mixture Types

Any liquid electrolyte solution unless there is association in the vapor phase.

Range

Vapor phase properties are described accurately up to medium pressures. Interaction parameters should be fitted in the range of operation.

The parameter requirements for he ELECNRTL property method are given in the following table, and in Parameters Required for General and Transport Property Models. For details about the model see *Physical Property Models*.

Parameters Required for the ELECNRTL Property Method

Thermodynamic Properties	**Models**	**Parameter Requirements**
Vapor mixture Fugacity coefficient, Density	Redlich-Kwong	TC, PC
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity correlation	CPIG or CPIGDP or CPIXP1, CPIXP2, CPIXP3
	Redlich-Kwong	TC, PC
Liquid mixture Fugacity coefficient, Gibbs energy	Electrolyte NRTL	Mol.: CPDIEC Ion: RADIUS Mol.-Mol.: NRTL Mol.-Ion, Ion-Ion: GMELCC, GMELCD GMELCE, GMELCN
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Mol. solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Mol. solute: (VC or VLBROC)

Thermodynamic Properties	Models	Parameter Requirements
Enthalpy, Entropy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	Solvent: TC, (DHVLWT or DHVLDP)
	Infinite dilution heat capacity / Criss-Cobble	Ions: CPAQ0 or Ions: IONTYP, S025C
	Electrolyte NRTL	Mol.: CPDIEC Ion: RADIUS Mol.-Mol.: NRTL Mol.-Ion, Ion-Ion: GMELCC, GMELCD GMELCE, GMELCN
Density	Rackett / Clarke	Mol.: TC, PC, (VC or VCRKT), (ZC or RKTZRA) Ion-ion: VLCLK
Solid pure (and mixture) Enthalpy, Entropy	General Pure Component Solid Heat Capacity	CPSP01 or CPSXP1 to CPSXP7
Density	General Pure Component Solid Molar Volume	VSPOLY

ENRTL-HF

The ENRTL-HF property method is similar to the ELECNRTL property method, except that it uses the HF equation of state as vapor phase model.

The HF equation of state predicts the strong association of HF in the vapor phase at low pressures. Association (mainly hexamerization) affects both vapor phase properties (for example, enthalpy and density) and liquid phase properties (for example, enthalpy).

A data package is available to accurately model vapor and liquid phases of HF and water mixtures in any proportion.

Mixture Types

The HF equation of state reliably predicts the strong association effects of HF in the vapor phase. The liquid can be any liquid electrolyte solution.

Range

Usage should not exceed pressures of 3 atm.

Parameters for the HF equation of state are built-in for temperatures up to 373 K. Parameters can be entered and regressed using the Aspen Physical Property

Data Regression System (DRS) if needed. For details about the model, see Electrolyte NRTL Activity Coefficient Model in *Physical Property Models*. For the parameter requirements for the electrolyte NRTL model, see the table labeled Parameters Required for the ELECNRTL Property Method (see ELECNRTL). For general and transport property parameter requirements, see the table Parameters Required for General and Transport Property Models.

ENRTL-HG

The ENRTL-HG property method is similar to theELECNRTL property method, except it uses the Helgeson model for standard properties calculations. The Helgeson model is a very accurate and flexible equation of state that calculates standard enthalpy, entropy, Gibbs free energy and volume for components in aqueous solutions. The Helgeson model should provide more accurate enthalpy and Gibbs free energy of process streams up to high temperatures and pressures. The model is also used to calculate Gibbs free energy for use in estimating chemical equilibrium constants (for both equilibrium and salt precipitation reactions) when they are missing. Equilibrium constants calculated using the Helgeson model have been found to be reasonably accurate and extrapolate well with respect to temperature.

Mixture Types

Any liquid electrolyte solution is acceptable, unless there is association in the vapor phase.

Range

Vapor phase properties are described accurately up to medium pressures. Interaction parameters should be fitted in the range of operation.

For parameter requirements for the electrolyte NRTL model, see the table labeled Parameters Required for the ELECNRTL Property Method (see ELECNRTL). For general and transport property parameter requirements, see the table labeled Parameters Required for General and Transport Property Models.

ENRTL-RK

The ENRTL-RK property method is based on the Unsymmetric Electrolyte NRTL property model. It uses:

- The Redlich-Kwong equation of state for vapor phase properties
- The unsymmetric reference state (infinite dilution in aqueous solution) for ionic species.
- Henry's law for solubility of supercritical gases.
- Unsymmetric Electrolyte NRTL method of handling zwitterions

ENRTL-RK reduces to the NRTL-RK property method when there are no ions in the system.

The ENRTL-RK method is identical to ELECNRTL for systems containing a single electrolyte. However, for mixed electrolyte systems, the ENRTL-RK method uses the mixing rules only to calculate interaction parameters, instead of calculating both interaction parameters and Gibbs free energy from mixing rules. Furthermore, the ENRTL-RK uses a single thermodynamics framework to calculate the activity coefficients, Gibbs free energy and enthalpy, instead of using separate models as in ELECNRTL.

Note: When using ENRTL-RK with solvents other than water, be sure you have good parameters for the model. There is a vast database of electrolyte parameters originally regressed for ELECNRTL with water, but these parameters are not valid for other solvents. If you do not have the parameters, consider using one of the electrolyte data packages.

Mixture Types

Any liquid electrolyte solution containing water, unless there is association in the vapor phase.

Range

Vapor phase properties are described accurately up to medium pressures. Interaction parameters should be fitted in the range of operation.

The parameter requirements for the ENRTL-RK property method are given in the following table, and in Parameters Required for General and Transport Property Models. For details about the model see Physical Property Models.

Note: Avoid using ENRTL-RK in the same problem with ELECNRTL, if the option **Require Engine to use special parameters for electrolyte method** is set on the **Setup | Calculation Options | Calculations** sheet (enabled by default). Doing so loads certain parameters designed for use with ELECNRTL but which may be inappropriate to use with ENRTL-RK.

Parameters Required for the ENRTL-RK Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Redlich-Kwong	TC, PC
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity correlation	CPIG or CPIGDP or CPIXP1, CPIXP2, CPIXP3
	Redlich-Kwong	TC, PC

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture Fugacity coefficient, Gibbs energy, Enthalpy, Entropy	Unsymmetric electrolyte NRTL	Mol.: CPDIEC Ion: RADIUS Mol.-Mol.: NRTL Mol.-Ion, Ion-Ion: GMENCC, GMENCD, GMENCE, GMENCN
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Mol. solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Mol. solute: (VC or VLBROC)
Enthalpy, Entropy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	Solvent: TC, (DHVLWT or DHVLDP)
	Infinite dilution heat capacity / Criss-Cobble	Ions: CPAQ0 or Ions: IONTYP, S025C
Density	Rackett / Clarke	Mol.: TC, PC, (VC or VCRKT), (ZC or RKTZRA) Ion-ion: VLCLK
Solid pure (and mixture) Enthalpy, Entropy	General Pure Component Solid Heat Capacity	CPSP01 or CPSXP1 to CPSXP7
Density	General Pure Component Solid Molar Volume	VSPOLY

ENRTL-SR

The ENRTL-SR property method is based on the Symmetric Electrolyte NRTL property model. It uses:

- The Redlich-Kwong equation of state vapor phase properties
- The symmetric reference state (pure fused salts) for ionic species.
- Henry's law for solubility of supercritical gases.
- Symmetric Electrolyte NRTL method of handling zwitterions

ENRTL-SR reduces to the NRTL-RK property method when there are no ions in the system.

ENRTL-SR uses a single thermodynamics framework to calculate the activity coefficients, Gibbs free energy, enthalpy, and entropy.

When using this property method, you must specify the **Symmetric** basis for activity coefficients of **Ionic components** on the **Input | Specifications** sheet of the **Chemistry** block it is used with.

Mixture Types

Any liquid electrolyte solution unless there is association in the vapor phase.

Range

Vapor phase properties are described accurately up to medium pressures. Interaction parameters should be fitted in the range of operation.

The parameter requirements for the ENRTL-SR property method are given in the following table, and in Parameters Required for General and Transport Property Models. For details about the model see Physical Property Models.

Parameters Required for the ENRTL-SR Property Method

Thermodynamic Properties	**Models**	**Parameter Requirements**
Vapor mixture Fugacity coefficient, Density	Redlich-Kwong	TC, PC
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity correlation	CPIG or CPIGDP or CPIXP1, CPIXP2, CPIXP3
	Redlich-Kwong	TC, PC
Liquid mixture Fugacity coefficient, Gibbs energy, Enthalpy, Entropy	Symmetric electrolyte NRTL	Mol.: CPDIEC Ion: RADIUS Mol.-Mol.: NRTL Mol.-Ion, Ion-Ion: GMENCC, GMENCD, GMENCE, GMENCN
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Mol. solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Mol. solute: (VC or VLBROC)

Thermodynamic Properties	**Models**	**Parameter Requirements**
Enthalpy, Entropy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	Solvent: TC, (DHVLWT or DHVLDP)
	Infinite dilution heat capacity / Criss-Cobble	Ions: CPAQ0 or Ions: IONTYP, S025C
Density	Rackett / Clarke	Mol.: TC, PC, (VC or VCRKT), (ZC or RKTZRA) Ion-ion: VLCLK
Solid pure (and mixture) Enthalpy, Entropy	General Pure Component Solid Heat Capacity	CPSP01 or CPSXP1 to CPSXP7
Density	General Pure Component Solid Molar Volume	VSPOLY

GPSWAT

The GPSWAT property method is based on the GPA Sour Water Equilibria Correlation and Computer Program (GPA RR-118) and is intended for use in gas treating and sour water systems. This method is an improvement over the SWEQ model, on which the APISOUR property method is based. The method extends the range of application of the SWEQ model from 68 – 284 °F (20 – 140 °C) to 68 – 600 °F (20 – 315 °C). It also allows for vapor non-ideality and permits simultaneous calculation of the equilibrium concentrations of inert components between an aqueous phase and a gas phase at total pressure up to 2000 psia with the sum of H_2S and CO_2 partial pressures not exceeding 1160 psia (Wilson and Eng, 1990).

This method:

- Uses the GPSWAT property models for vapor and liquid fugacity coefficient of 18 components listed below.
- Is designed for gas treating and sour water systems containing mainly water, ammonia, hydrogen sulfide and carbon dioxide.
- Is applicable from 68 to 600 °F (20 to 315 °C) and up to 2000 psia.
- Is limited to ammonia concentrations up to 40 mole percent and combined CO_2 and H_2S partial pressure up to 1160 psia, and up to 3 wt% caustic.
- Uses the SRK method to calculate fugacity coefficients of other components.
- Uses SRK to calculate other properties. All relevant option codes of the models used by SRK apply.
- Does not require any user-specified parameters.

- Does not depend on any CHEMISTRY input. Do not specify Chemistry ID in any Electrolyte calculation options field.

The components for which the GPSWAT model calculates fugacity coefficients are:

Alias	**Name**
H2O	WATER
NH3	AMMONIA
CO2	CARBON-DIOXIDE
H2S	HYDROGEN-SULFIDE
CH4	METHANE
C2H6	ETHANE
C3H8	PROPANE
C4H10-1	N-BUTANE
C4H10-2	ISOBUTANE
C5H12-1	N-PENTANE
C5H12-2	2-METHYL-BUTANE
H2	HYDROGEN
N2	NITROGEN
CO	CARBON-MONOXIDE
CS2	CARBON-DISULFIDE
COS	CARBONYL-SULFIDE
CH4S	METHYL-MERCAPTAN
C2H6S-1	ETHYL-MERCAPTAN

References

Grant M. Wilson, Wayne W. Y. Eng, Wiltec Research Co., "GPA Sour Water Equilibria Correlation and Computer Program." GPA Research Report RR-118, Gas Processors Association, Feb. 1990.

Paul C. Gillespie, W. Vincent Wilding, Grant M. Wilson, “Vapor-Liquid Equilibrium Measurements on the Ammonia-Water System from 313K to 589K,” GPA Research Report RR-90, Gas Processors Association, Oct. 1985.

PITZER

The PITZER property method is based on an aqueous electrolyte activity coefficient model. It has no overlap with other activity coefficient models. It can accurately calculate the behavior of aqueous electrolyte solutions with or without molecular solutes up to 6 molal ionic strength.

Many interaction parameters from regression of experimental data are included in databanks and data packages (for details, see Overview of Aspen Physical Property Methods).

You can model the solubility of supercritical gases using Henry's law. Henry coefficients are available from the Aspen Physical Property System databanks (see Overview of Aspen Physical Property Methods).

Heats of mixing are calculated using the Pitzer model.

The Redlich-Kwong-Soave equation of state is used for the vapor phase fugacity coefficient. All other vapor phase properties are assumed ideal. Redlich-Kwong-Soave cannot model association behavior in the vapor phase (for example, carboxylic acids or HF). For carboxylic acids, choose a non-electrolyte activity coefficient model with Hayden-O'Connell or Nothnagel; for HF choose ENRTL-HF or WILS-HF.

Mixture Types

You can use the Pitzer model for any aqueous electrolyte solution up to 6 molal ionic strength, not showing association in the vapor phase.

Important: PITZER cannot be used for systems with any other solvent or mixed solvents. Any non-water molecular components are considered solutes and treated as Henry components.

Range

Vapor phase fugacities are described accurately up to medium pressures. Interaction parameters should be fitted in the range of operation.

The parameter requirements for the PITZER property method are given in the following table, and the table labeled Parameters Required for General and Transport Property Models. For details about the model, see *Physical Property Models*.

Parameters Required for the PITZER Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Redlich-Kwong-Soave	TC, PC, OMEGA
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity correlation	CPIG or CPIGDP or CPIXP1, CPIXP2, CPIXP3
	Redlich-Kwong	TC, PC, OMEGA

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture Fugacity coefficient, Gibbs energy	Pitzer	Cation-anion: GMPTB0, GMPTB1, GMPTB2, GMPTB3, GMPTC Cation-cation: GMPTTH Anion-anion: GMPTTH Cation1-cation2-common anion: GMPTPS Anion1-anion2-common cation: GMPTPS Molecule-ion, Mol. – Mol.: GMPTB0, GMPTB1, GMPTC
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Mol. solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Mol. solute: (VC or VLBROC)
Enthalpy, Entropy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	Solvent: TC, (DHVLWT or DHVLDP)
	Infinite dilution heat capacity / Criss-Cobble	Ions: CPAQ0 or Ions: IONTYP, S025C
	Pitzer	Cation-anion: GMPTB0, GMPTB1, GMPTB2, GMPTB3, GMPTC Cation-cation: GMPTTH Anion-anion: GMPTTH Cation1-cation2-common anion: GMPTPS Anion1-anion2-common cation: GMPTPS Molecule-ion, Mol. – Mol.: GMPTB0,GMPTB1,GMPTC
Density	Rackett / Clarke	Mol.: TC, PC, (VC or VCRKT), (ZC or RKTZRA) Ion-ion: VLCLK
Solid pure (and mixture) Enthalpy, Entropy	General Pure Component Solid Heat Capacity	CPSP01 or CPSXP1 to CPSXP7
Density	General Pure Component Solid Molar Volume	VSPOLY

B-PITZER

The B-PITZER property method is based on the simplified Pitzer aqueous electrolyte activity coefficient model, which neglects third order interactions. It can predict the behavior of aqueous electrolyte solutions up to 6 molal ionic strength. It is not as accurate as ELECNRTL or PITZER with fitted parameters. However, it is better than using these property methods without interaction parameters.

You can model the solubility of supercritical gases using Henry's law. Henry coefficients are available from the Aspen Physical Property System databanks (see Overview of Aspen Physical Property Methods).

Heats of mixing are calculated using the Bromley-Pitzer model.

The Redlich-Kwong-Soave equation of state is used for the vapor phase fugacity coefficient. All other vapor phase properties are assumed ideal. Redlich-Kwong-Soave cannot model association behavior in the vapor phase (for example with carboxylic acids or HF). For carboxylic acids, choose a non-electrolyte activity coefficient model with Hayden-O'Connell or Nothnagel; for HF choose ENRTL-HF or WILS-HF.

Mixture Types

You can use the B-PITZER model for any aqueous electrolyte solution up to 6M ionic strength, not showing association in the vapor phase.

Range

Vapor phase fugacities are described accurately up to medium pressures. Interaction parameters should be fitted in the range of operation.

The parameter requirements for the B-PITZER property method are given in the following table, and the table labeled Parameters Required for General and Transport Property Models. For details about the model, see Pitzer Activity Coefficient Model in *Physical Property Models*.

Parameters Required for the B-PITZER Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture Fugacity coefficient, Density	Redlich-Kwong-Soave	TC, PC, OMEGA

Thermodynamic Properties	**Models**	**Parameter Requirements**
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity correlation	CPIG or CPIGDP or CPIXP1, CPIXP2, CPIXP3
	Redlich-Kwong	TC, PC, OMEGA
Liquid mixture Fugacity coefficient, Gibbs energy	Bromley-Pitzer	Ionic: GMBPB, GMBPD Optional: Cation-anion: GMPTB0, GMPTB1, GMPTB2, GMPTB3 Cation-cation: GMPTTH Anion-anion: GMPTTH Molecule-ion, Mol.-Mol.: GMPTB0, GMPTB1
	General Pure Component Liquid Vapor Pressure	PLXANT
	Henry's constant	Solvent: VC, Mol. solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Mol. solute: (VC or VLBROC)
Enthalpy, Entropy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	Solvent: TC, (DHVLWT or DHVLDP)
	Infinite dilution heat capacity / Criss-Cobble	Ions: CPAQ0 or Ions: IONTYP, S025C
	Bromley-Pitzer	Ionic: GMBPB, GMBPD Optional: Cation-anion: GMPTB0, GMPTB1, GMPTB2, GMPTB3 Cation-cation:GMPTTH Anion-anion: GMPTTH Molecule-ion, Mol.-Mol.: GMPTB0, GMPTB1
Density	Rackett / Clarke	Mol.: TC, PC, (VC or VCRKT), (ZC or RKTZRA) Ion-ion: VLCLK
Solid pure (and mixture) Enthalpy, Entropy	General Pure Component Solid Heat Capacity	CPSP01 or CPSXP1 to CPSXP7
Density	General Pure Component Solid Molar Volume	VSPOLY

PITZ-HG

The PITZ-HG property method is similar to the PITZER property method, except it uses the Helgeson model for standard properties calculations. The Helgeson model is a very accurate and flexible equation of state that calculates standard enthalpy, entropy, Gibbs free energy and volume for components in aqueous solutions. The Helgeson model should provide more accurate enthalpy and Gibbs free energy of process streams up to high temperatures and pressures. The Helgeson model is also used to calculate Gibbs free energy for use in estimating chemical equilibrium constants (for both equilibrium and salt precipitation reactions) when they are missing. Equilibrium constants calculated using the Helgeson model have been found to be reasonably accurate and extrapolate well with respect to temperature.

Mixture Types

You can use this property method for any aqueous electrolyte solution up to 6M ionic strength, not showing association in the vapor phase.

Range

Vapor phase fugacities are described accurately up to medium pressures. Interaction parameters should be fitted in the range of operation.

The parameter requirements for the PITZ-HG property method are given in the table labeled Parameters Required for the PITZER Property Method (see PITZER), and the table labeled Parameters Required for General and Transport Property Models. For details about the model, see *Physical Property Models*.

OLI Property Method

The OLI property method provides accurate results for the thermodynamic and transport properties of aqueous mixtures and associated immiscible organic mixtures, using Aspen OLI.

Aspen OLI is a software solution that enables process engineers to quickly and reliably perform process modeling and analysis of aqueous electrolyte systems. Together with Aspen Physical Property System-based solids and electrolytes modeling technology, Aspen OLI Interface provides the chemical process industries with comprehensive capability to model aqueous electrolyte systems over the complete concentration range, including most of the elements in the Periodic Table.

Models

All models require the OLI license.

- GLMXOLI: OLI model for liquid mixture molar Gibbs energy
- GMOLI: OLI model for liquid phase activity coefficient
- GVMXOLI: OLI model for vapor mixture molar Gibbs energy

- HLMXOLI: OLI model for liquid mixture molar enthalpy
- HSMXOLI: OLI model for solid mixture molar enthalpy
- HVMXOLI: OLI model for vapor mixture molar enthalpy
- MULMXOLI: OLI model for liquid mixture viscosity
- PHILOLI: Liquid pure component fugacity coefficient calculated from the OLI model
- PHLMXOLI: OLI model for liquid fugacity coefficient of a component in a mixture
- PHVMXOLI: OLI model for vapor fugacity coefficient of a component in a mixture
- SLMXOLI: OLI model for liquid mixture molar entropy
- SVMXOLI: OLI model for vapor mixture molar entropy
- VLMXOLI: OLI model for liquid mixture molar volume
- VVMXOLI: OLI model for vapor mixture molar volume

Licensing Structure

Aspen OLI consists of two parts:

- Aspen OLI Interface provided by AspenTech. The interface is included with Aspen Plus and Aspen Properties and is provided without additional license.
- OLI Alliance Suite for Aspen OLI licensed by OLI Systems.

Existing customers of Aspen OLI are entitled to the OLI license automatically. However, new customers of Aspen OLI will need to sign a contract with OLI Systems. OLI Systems will provide the necessary software license manager, Hardlock security key and serial number required to access the OLI Alliance Suite for Aspen OLI.

To obtain a license, please contact OLI Systems:

OLI Systems, Inc.
American Enterprise Park
108 American Road
Morris Plains, NJ 07950
USA
Phone (973) 539-4996
Fax (973) 539-5922

http://www.olisystems.com

Software Installation

Installation of Aspen OLI requires these steps:

1. Contact OLI Systems to obtain the OLI Hardlock security key, serial number, and password for installing the OLI Alliance Suite as part of the continued licensing of Aspen OLI.

2. Install the Aspen OLI Interface, a sub-feature of the AES Installation. When this installation is complete, you will have installed all of the components required within the Aspen framework to support the OLI Engine.
3. Install the OLI Engine in order to complete the installation of Aspen OLI. Download this from OLI using the **Downloads** link at their web site, linked above. During the installation, you will be asked to supply the serial number obtained in step 1.

   If multiple versions of Aspen Plus are installed, you can link all of them using the OLI Alliance Software Config Tool located in the Start menu under **All Programs | OLI Systems | OLI Engine <version> for Aspen Plus | Tools**. Click **Link All** in this tool to link all the Aspen Plus versions to the desired version of the OLI engine.
4. Finally, you will need to use the OLI Hardlock security key and serial number obtained in step 1 to enable OLI's license manager.

Using Aspen OLI with Apparent Component Electrolyte Systems

Aspen OLI is capable of modeling electrolyte simulations in apparent approach, but the algorithm OLI uses for generating the apparent components from the underlying true composition is different from that of Aspen Properties. When there are multiple ways of representing the solution composition as apparent components, OLI may give different (but equivalent) apparent components from other property methods.

Solids

The OLI property method can be used with both conventional inert solids (CISOLID) and nonconventional solids (NCSOLID). The selected nonconventional method will be used to calculate enthalpy of nonconventional solids.

General and Transport Property Model Parameter Requirements

The following table describes the general and transport property models used and their parameter requirements for activity coefficient-based electrolyte property methods.

Parameters Required for General and Transport Property Models

General

Property/Purpose	Parameter Requirements
Mass balance, Conversion Mass-basis↔ Mole-basis	MW
Enthalpy of reaction	Solvents, Mol. solutes: DHFORM Solids,Salts: (DHSFRM or CPSXP1 to CPSXP7) Ions: DHAQFM
Gibbs energy of reaction	Solvents, Mol. solutes: DGFORM Solids,Salts: (DGSFRM or CPSXP1 to CPSXP7) Ions: DGAQFM

Transport Properties

Property	Models	Parameter Requirements
Vapor mixture Viscosity	General Pure Component Vapor Viscosity	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal conductivity	General Pure Component Vapor Thermal Conductivity	MW or KVDIP
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	General Pure Component Liquid Surface Tension, Onsager-Samaras	Solv., Mol.sol.: (TC, PC, OMEGA) or SIGDIP Ion: CHARGE
Liquid mixture Viscosity	General Pure Component Liquid Viscosity, Jones-Dole	Solv., Mol.sol.: MULAND or MULDIP Ion: IONMUB, IONMOB
Thermal Conductivity	General Pure Component Liquid Thermal Conductivity, Riedel	Solv., Mol.sol.: (MW, TC, TB) or KLDIP Ion: IONRDL
Diffusivity	Wilke-Chang, Nernst-Hartley	Solv., Mol.sol.: MW, VB Ion: CHARGE, IONMOB

Note: For surface tension and liquid mixture properties, the second method is used only for rigorous electrolyte properties.

Solids Handling Property Method

The SOLIDS property method is designed for many kinds of solids processing:

- Coal processing
- Pyrometallurgical processes
- Miscellaneous other solids processing (such as starch and polymers)

The properties of solids and fluid phases cannot be calculated with the same type of models. Therefore the components are distributed over the substreams of types MIXED, CISOLID and NC and their properties are calculated with appropriate models.

During the mechanical processing of raw materials (ore, coal, wood), physical properties can often be handled as nonconventional components with an overall density and an overall heat capacity. The characterization of nonconventional components and the specification of property models is discussed in the Defining a Non-Conventional Component in the help. Details on nonconventional property methods are given in Nonconventional Component Enthalpy Calculation in Overview of Aspen Physical Property Methods. Details on nonconventional property models are given in *Physical Property Models*.

When the solids are decomposed into individual components (for example, to selectively undergo chemical reactions), they normally occur in the CISOLID substream. The property models for these components are pure component property models of the polynomial type. The components are not in phase equilibrium with the fluid components. Some examples are coal dust in air, burning carbon, and sand in water. It is also possible to place conventional solids in the MIXED substream.

In pyrometallurgical applications, a CISOLID component can be in simultaneous phase and chemical equilibrium. This can happen only in the RGIBBS model, an equilibrium reactor based on Gibbs energy minimization. Under other conditions, the CISOLID component can undergo reactions but not phase equilibrium. As another exception, homogeneous solid mixture phases can occur in the same reactor. The nonideality of solid mixtures can be handled using activity coefficient models. To distinguish a solid mixture from single CISOLID components, they are placed in the MIXED substream.

In pyrometallurgical applications, many phases can occur simultaneously. These phases may need to be treated with different activity coefficient models (use the SOLIDS property method). For details, see *Getting StartedModeling Processes with Solids*.

Fluid components always occur in the MIXED substream. They are treated with the same fluid phase models as discussed in IDEAL. If non-ideality in the liquid phase occurs, the ideal activity coefficient model can be replaced.

Permanent gases may be dissolved in the liquid. You can model them using Henry's law, which is valid at low concentrations.

Hydrometallurgical applications cannot be handled by the SOLIDS property method. Use an electrolyte property method.

The transport property models for the vapor phase are all well suited for ideal gases. The transport property models for the liquid phase are empirical equations for fitting of experimental data.

The following table lists the models used in the SOLIDS property method and their parameter requirements. For details on these models, see *Physical Property Models*.

Parameters Required for the SOLIDS Property Method

General

Property/Purpose	**Parameter Requirements**
Mass balance, Conversion Mass-basis↔ Mole-basis	MW
Conversion Stdvol-basis↔ Mole-basis	VLSTD
Free-water option: solubility of water in organic phase	WATSOL
Enthalpy of reaction	DHFORM, (DHSFRM or CPSXP1 to CPSXP7)
Gibbs energy of reaction	DGFORM, (DGSFRM or CPSXP1 to CPSXP7)

Thermodynamic Properties

Property	**Models**	**Parameter Requirements**
Vapor pure and mixture Fugacity Coefficient	Ideal gas law	

Property	Models	Parameter Requirements
Enthalpy, Entropy, Gibbs energy	General pure component ideal gas heat capacity correlation	CPIG or CPIGDP or CPIXP1, CPIXP2, CPIXP3
Density	Ideal gas law	
Liquid pure and mixture Fugacity Coefficient, Gibbs energy	General Pure Component Liquid Vapor Pressure	PLXANT or CPIXP1, CPIXP2
	Ideal liquid activity coefficient	—
	Henry's constant	Solvent: VC, Solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Solute: (VC or VLBROC)
Enthalpy, Entropy	General pure component ideal gas heat capacity	CPIG or CPIGDP
	General Pure Component Heat of Vaporization	TC, (DHVLWT or DHVLDP)
	General Pure Component Liquid Heat Capacity	CPLDIP or CPLXP1, CPLXP2
Density	Constant Volume, Ideal mixing	VLCONS
Solid pure (and mixture) Fugacity Coefficient, Gibbs energy	Extended solid Antoine vapor pressure	PSXANT or PSANT
	Barin correlation	CPSXP1 to CPSXP7
	Ideal liquid activity coefficient	—
Enthalpy, Entropy	General Pure Component Solid Heat Capacity	CPSP01 or CPSXP1 to CPSXP7
Density	General Pure Component Solid Molar Volume	VSPOLY

Transport Properties

Property	Models	Parameter Requirements
Vapor pure and mixture Viscosity	General Pure Component Vapor Viscosity	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal conductivity	General Pure Component Vapor Thermal Conductivity	MW or KVDIP

Property	Models	Parameter Requirements
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	General Pure Component Liquid Surface Tension	(TC, PC, OMEGA) or SIGDIP
Liquid pure and mixture Viscosity	General Pure Component Liquid Viscosity	MULAND or MULDIP
Thermal Conductivity	General Pure Component Liquid Thermal Conductivity	(MW, TC, TB) or KLDIP
Diffusivity	Wilke-Chang	MW, VB
Solids pure Thermal Conductivity	Solids polynomial	KSPOLY

Steam Tables

The following table lists the names of the steam table property methods available in Aspen Physical Property System.

Steam tables can calculate all thermodynamic properties for systems containing pure water or steam. For mixtures of water and other components, refer to the beginning of this chapter for more help.

For process calculations, the accuracy of all three models is adequate. The STEAM-TA method is made up of different correlations covering different regions of the P-T space. These correlations do not provide continuity at the boundaries, which can lead to convergence problems and predict wrong trends. STMNBS2 can also have this problem. STEAMNBS does not have this problem and it extrapolates better, so it may be a better choice when there are not other considerations. For similar reasons, it may be better to use STEAMNBS with property methods such as SRK that calculate water properties from the free-water property method.

The transport property models for both property methods are from the International Association for Properties of Steam (IAPS).

All models have built-in parameters. For details, see ASME Steam Tables, NBS/NRC Steam Tables, and IAPWS-95 Steam Tables in *Physical Property Models*.

Steam Tables Property Methods

Property Method Name	Models (Steam Tables)
STEAM-TA	ASME 1967
STEAMNBS/STMNBS2	NBS/NRC 1984
IAPWS-95	IAPWS 1995
IF97	IAPWS Industrial Formulation 1997

Common models

IAPS surface tension
IAPS viscosity for water and steam
IAPS thermal conductivity for water and steam

STEAM-TA

The STEAM-TA property method uses the:

- 1967 ASME steam table correlations for thermodynamic properties
- International Association for Properties of Steam (IAPS) correlations for transport properties

Use this property method for pure water and steam. The Aspen Physical Property System uses STEAM-TA as the default property method for the free-water phase, when free-water calculations are performed.

For process calculations, the accuracy of the models is adequate. The STEAM-TA method is made up of different correlations covering different regions of the P-T space. These correlations do not provide continuity at the boundaries, which can lead to convergence problems and predict wrong trends. For some applications STEAMNBS may be a better choice.

Range

Use the STEAM-TA property method for pure water and steam with temperature ranges of 273.15 K to 1073 K. The maximum pressure is 1000 bar.

STEAMNBS/STMNBS2

The STEAMNBS/STMNBS2 property methods use:

- 1984 NBS/NRC steam table correlations for thermodynamic properties
- International Association for Properties of Steam (IAPS) correlations for transport properties

The STMNBS2 uses the same equations as STEAMNBS but with a different root search method.

Use these property methods for pure water and steam, and in particular for the free-water phase.

Range

Use the STEAMNBS/STMNBS2 property methods for pure water and steam with temperature ranges of 273.15 K to 2000 K. The maximum pressure is over 10000 bar. The STEAMNBS method is recommended for use with the SRK, BWRS, MXBONNEL and GRAYSON2 property methods.

RTOSTM

The RTOSTM method is an older version of STMNBS2. It is intended for use only with legacy projects from RT-Opt which were tuned to use this method.

IAPWS-95 Property Method

The IAPWS-95 property method uses the

- 1995 IAPWS steam table correlations for thermodynamic properties

Use this property method for pure water and steam, in particular for the free-water phase.

IAPWS-95 is the current standard steam table from the International Association for the Properties of Water and Steam. It replaces the previous 1984 formulation (IAPS-84) implemented in Aspen Plus as STEAMNBS and STMNBS2. IAPWS-95 overcomes several shortcomings of IAPS-84, including weaknesses near the critical point (regarding the phase boundary and in its derivative properties such as isothermal compressibility) and when extrapolating beyond its range of validity.

The IAPWS-95 formulation is in the form of a fundamental equation explicit in Helmholtz free energy. The residual part of the Helmholtz free energy was fitted to the following properties: (a) thermal properties of the single-phase region ($p\rho T$) and of the vapor-liquid phase boundary ($p\rho'\rho''T$), including the phase-equilibrium conditions (Maxwell criterion), and (b) the caloric properties - specific isochoric heat capacity, specific isobaric heat capacity, speed of sound, differences in the specific enthalpy and in the specific internal energy, Joule-Thomson coefficient, and isothermal throttling coefficient.

Region & Property	Estimated Uncertainty

Liquid – density	±0.001% to ±0.02%
Liquid – speed of sound	±0.03% to ±0.2%
Liquid – isobaric heat capacity	±0.1%
Liquid at ambient pressure – density	≤0.0001%
Liquid at ambient pressure – speed of sound	±0.005%
Gas – density	±0.03% to ±0.05%
Gas – speed of sound	±0.15%
Gas – isobaric heat capacity	±0.2%

Range

The IAPWS-95 formation covers a validity range for temperatures from the melting line (lowest temperature 251.2 K at 209.9 MPa) to 1273 K and pressures up to 1000 MPa. In this entire range of validity, it represents even the most accurate data to within their experimental uncertainty.

In the stable fluid region, the IAPWS-95 formulation can be extrapolated beyond the limits of validity listed above. The model behaves reasonably well when extrapolated to pressures up to 2000 MPa and temperatures up to 3000 K as long as the conditions are in the fluid region (less than melting pressure at specified temperature, and greater than melting temperature at specified pressure).

IF97

The IF97 property method uses the IAPWS Industrial Formulation 1997 correlation for thermodynamic properties of water and steam.

The industrial formulation is a polynomial model which matches IAPWS-95 to a high degree of accuracy within its range of applicability. This model provides equations which allow properties to be computed very quickly, without the need for iterative calculations. While the IAPWS-95 is the current standard for scientific use, the industrial formulation is more computationally efficient and can be used where computation speed is more of the essence.

Use this property method for pure water and steam, particularly for the free-water phase.

Range

IF97 covers temperatures from 0 to 800 °C (273.15 to 1013.75 K) at pressures up to 1000 bar, and from 800 to 2000 °C (1073.15 to 2273.15 K) at pressures up to 500 bar as shown in the figure below.

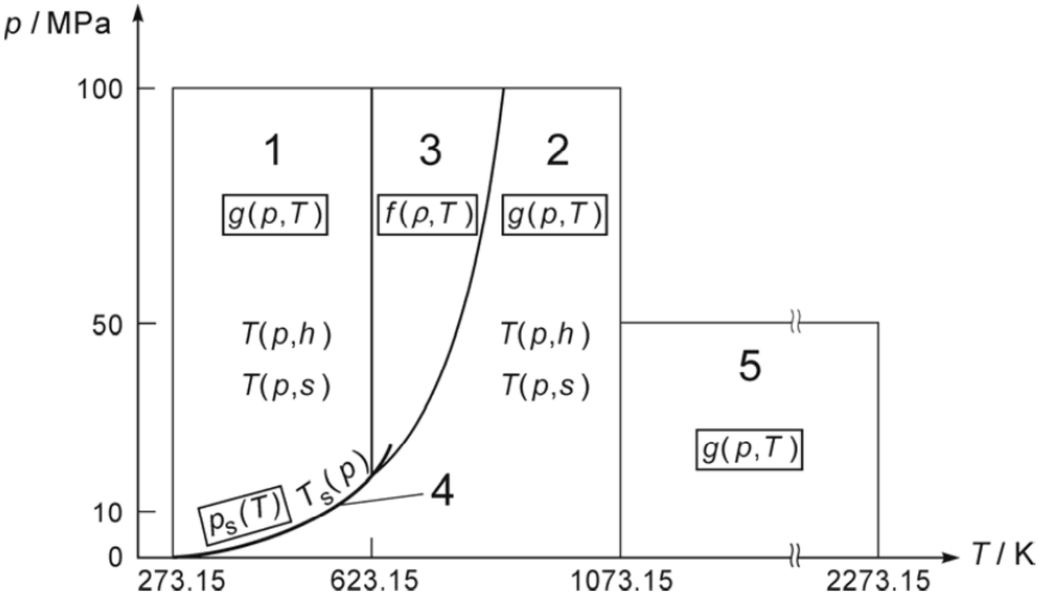


Diagram of five regions, from the International Association for the Properties of Water and Steam [1]

The space below 800 °C is divided into four regions which use different basic equations. Region 1 is liquid water below 350 °C. Region 2 is water vapor below 350 °C and at higher temperatures below a dividing line which is roughly isentropic around 5.1 kJ/kg-K. Region 3 is the region near and above the critical point (between regions 1 and 2), and region 4 is the vapor-liquid line below 350 °C. The space above 800 °C is a fifth region, also with a separate equation.

Region	Basic equation form
1	$G(p,T)$
2	$G(p,T)$
3	$A(\rho,T)$
4	$p_{sat}(T)$
5	$G(p,T)$

Where *G* represents Gibbs free energy, *A* represents Helmholtz free energy, *p* represents pressure, *T* represents temperature, and the subscript *sat* represents saturation.

Other properties can be calculated as combinations of the free energy properties and their derivatives.

In addition to the equations described above, the basic equation for region 1 is used to calculate liquid properties in the metastable superheated-liquid region close to the saturation line, and alternate equations are used for vapor properties in the metastable vapor region. Yet more equations are used to define the region boundaries. Most of the actual equations are polynomials with many terms, and are omitted here; see [1] for the precise equation forms.

IF97 uses LibIF97 library licensed from [2].

Reference

1. International Association for the Properties of Water and Steam, Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam. Lucerne, Switzerland, August 2007.
2. H.-J. Kretzschmar, M. Kunick, S. Herrmann, I. Stöcker, M. Nicke, Property Libraries for Working Fluids used in Power Engineering. Zittau/Goerlitz University of Applied Sciences, Department of Technical Thermodynamics, Zittau, Germany (1997-2015), available at www.thermodynamics-zittau.de

3 Property Calculation Methods and Routes

In the Aspen Physical Property System the methods and models used to calculate thermodynamic and transport properties are packaged in property methods. Each property method contains all the methods and models needed for a calculation. A unique combination of methods and models for calculating a property is called a *route*.

Physical Property Methods in Using the Properties Environment in the help describes the property methods available in the Aspen Physical Property System, provides guidelines for choosing an appropriate property method for your calculation, and describes how to modify property methods to suit your calculation needs by replacing property models.

This chapter discusses:

- Major, subordinate, and intermediate properties in the Aspen Physical Property System
- Calculation methods available
- Routing concepts
- Property models available
- Tracing routes
- Modifying and creating property methods
- Modifying and creating routes

Introduction

Most properties are calculated in several steps. An example is the calculation of the fugacity coefficient of a component in a liquid mixture:

$$\phi_i^l = \gamma_i \phi_i^{*,l} \qquad (1)$$

Where:

$$\phi_i^{*,l} = \frac{\phi_i^{*,v} p_i^{*,v}}{p} \qquad (2)$$

Equations 1 and 2 are both derived from thermodynamics. The equations relate the properties of interest (φ_i^l,$\varphi_i^{*,l}$)to other properties (γ_i, $\varphi_i^{*,v}$, $p_i^{*,l}$) and state variables (x_i, p). In general, this type of equation is derived from universal scientific principles. These equations are called *methods*.

In the computation of the liquid mixture fugacity, you need to calculate:

- Activity coefficient (γ_i)
- Vapor pressure ($p_i^{*,l}$)
- Pure component vapor fugacity coefficient

This type of property is usually calculated using equations that depend on universal parameters like $T_c$and p_c; state variables, such as T and p; and correlation parameters. The use of correlation parameters makes these equations much less universal and more subjective than methods. For distinction, we call them *models*. Often several models exist to calculate one property. For example, to calculate γ_i you can use the NRTL, UNIQUAC, or UNIFAC model.

The reason for treating models and methods separately is to allow for maximum flexibility in property calculations. Therefore the descriptions provided should help show the flexibility of the Aspen Physical Property System, rather than constitute definitions. For detailed descriptions and lists of available methods and models, see Methods and Routes and Models.

A complete calculation route consists of a combination of methods and models. A number of frequently used routes have been defined in the Aspen Physical Property System. Routes that belong logically together have been grouped to form property methods. For more about property methods, see Property Method Descriptions. Routes are discussed in detail in Routes and Models.

To choose a different calculation route for a given property route than what is defined in a property method, you can exchange routes or models in property methods (See Modifying and Creating Property Methods).

For a specific property, there are many choices of models and methods used to build a route. Therefore the Aspen Physical Property System does not contain all possible routes as predefined routes. However you can freely construct calculation routes according to your needs. This is a unique feature of the Aspen Physical Property System. Modifying and creating new routes from existing methods, routes and models, and using them in modified or new property methods is explained in Modifying and Creating Routes.

Physical Properties in the Aspen Physical Property System

The following properties may be required by Aspen Physical Property System calculations:

- Thermodynamic Properties
- Fugacity coefficients (for K values)
- Enthalpy
- Entropy
- Gibbs energy
- Molar volume
- Transport Properties
- Viscosity
- Thermal conductivity
- Diffusion coefficient
- Surface tension

The properties required by unit operation models in the Aspen Physical Property System are called *major properties* and are listed in the table labeled Major Properties in the Aspen Physical Property System. A major property may depend on other major properties. In addition, a major property may depend on other properties that are not major properties. These other properties can be divided into two categories: subordinate properties and intermediate properties.

Subordinate properties may depend on other major, subordinate or intermediate properties, but are not directly required for unit operation model calculations. Examples of subordinate properties are enthalpy departure and excess enthalpy. The table labeled Subordinate Properties in the Aspen Physical Property System lists the subordinate properties.

Intermediate properties are calculated directly by property models, rather than as fundamental combinations of other properties. Common examples of intermediate properties are vapor pressure (calculated by performing a bubble point flash) and activity coefficients. The table labeled Intermediate Properties in the Aspen Physical Property System lists the intermediate properties.

Major and subordinate properties are obtained by a method evaluation. Intermediate properties are obtained by a model evaluation.

Major Properties in the Aspen Physical Property System

Property Name	Symbol	Description
PHIV	$\varphi_i^{*,v}$	Vapor pure component fugacity coefficient
PHIL	$\varphi_i^{*,l}$	Liquid pure component fugacity coefficient
PHIS	$\varphi_i^{*,s}$	Solid pure component fugacity coefficient
PHIVMX	φ_i^{v}	Vapor fugacity coefficient of a component in a mixture
PHILMX	φ_i^{l}	Liquid fugacity coefficient of a component in a mixture
PHISMX	φ_i^{s}	Solid fugacity coefficient of a component in a mixture
HV	$H_i^{*,v}$	Vapor pure component molar enthalpy
HL	$H_i^{*,l}$	Liquid pure component molar enthalpy
HS	$H_i^{*,s}$	Solid pure component molar enthalpy
HVMX	H_m^{v}	Vapor mixture molar enthalpy
HLMX	H_m^{l}	Liquid mixture molar enthalpy
HSMX	H_m^{s}	Solid mixture molar enthalpy
GV	$\mu_i^{*,v}$	Vapor pure component molar Gibbs free energy
GL	$\mu_i^{*,l}$	Liquid pure component molar Gibbs free energy
GS	$\mu_i^{*,s}$	Solid pure component molar Gibbs free energy
GVMX	G_m^{v}	Vapor mixture molar Gibbs free energy
GLMX	G_m^{l}	Liquid mixture molar Gibbs free energy
GSMX	G_m^{s}	Solid mixture molar Gibbs free energy
SV	$S_i^{*,v}$	Vapor pure component molar entropy
SL	$S_i^{*,l}$	Liquid pure component molar entropy
SS	$S_i^{*,s}$	Solid pure component molar entropy
SVMX	S_m^{v}	Vapor mixture molar entropy
SLMX	S_m^{l}	Liquid mixture molar entropy
SSMX	S_m^{s}	Solid mixture molar entropy
VV	$V_i^{*,v}$	Vapor pure component molar volume

Property Name	Symbol	Description
VL	$V_i^{*,l}$	Liquid pure component molar volume
VS	$V_i^{*,s}$	Solid pure component molar volume
VVMX	V_m^v	Vapor mixture molar volume
VLMX	V_m^l	Liquid mixture molar volume
VSMX	V_m^s	Solid mixture molar volume
MUV	$\eta_i^{*,v}$	Vapor pure component viscosity
MUL	$\eta_i^{*,l}$	Liquid pure component viscosity
MUVMX	η^v	Vapor mixture viscosity
MULMX	η^l	Liquid mixture viscosity
KV	$\lambda_i^{*,v}$	Vapor pure component thermal conductivity
KL	$\lambda_i^{*,l}$	Liquid pure component thermal conductivity
KS	$\lambda_i^{*,s}$	Solid pure component thermal conductivity
KVMX	λ^v	Vapor mixture thermal conductivity
KLMX	λ^l	Liquid mixture thermal conductivity
KSMX	λ^s	Solid mixture thermal conductivity
DV	D_{ij}^v	Vapor binary diffusion coefficient
DL	D_{ij}^l	Liquid binary diffusion coefficient
DVMX	D_i^v	Vapor diffusion coefficient of a component in a mixture
DLMX	D_i^l	Liquid diffusion coefficient of a component in a mixture at infinite dilution
SIGL	$\sigma_i^{*,l}$	Pure component surface tension
SIGLMX	σ^l	Mixture surface tension

Subordinate Properties in the Aspen Physical Property System

Property Name	Symbol	Description
DHV	$H_i^{*,v}-H_i^{*,ig}$	Vapor pure component molar enthalpy departure

Property Name	Symbol	Description
DHL	$H_i^{*,l} - H_i^{*,ig}$	Liquid pure component molar enthalpy departure
DHS	$H_i^{*,s} - H_i^{*,ig}$	Solid pure component molar enthalpy departure
DHVMX	$H_m^v - H_m^{ig}$	Vapor mixture molar enthalpy departure
DHLMX	$H_m^l - H_m^{ig}$	Liquid mixture molar enthalpy departure
DHSMX	$H_m^s - H_m^{ig}$	Solid mixture molar enthalpy departure
DHVPC	$H_i^{*,v}(p) - H_i^{*,v}(p_i^*)$	Vapor pure component molar enthalpy departure pressure correction
DHLPC	$H_i^{*,l}(p) - H_i^{*,s}(p_i^*)$	Liquid pure component molar enthalpy departure pressure correction
DHSPC	$H_i^{*,l}(p) - H_i^{*,s}(p_i^*)$	Solid pure component molar enthalpy departure pressure correction
DGV	$\mu_i^{*,v} - \mu_i^{*,ig}$	Vapor pure component molar Gibbs energy departure
DGL	$\mu_i^{*,l}-\mu_i^{*,ig}$	Liquid pure component molar Gibbs energy departure
DGS	$\mu_i^{*,s}-\mu_i^{*,ig}$	Solid pure component molar Gibbs energy departure
DGVMX	$G_m^v - G_m^{ig}$	Vapor mixture molar Gibbs energy departure
DGLMX	$G_m^l - G_m^{ig}$	Liquid mixture molar Gibbs energy departure
DGSMX	$G_m^s - G_m^{ig}$	Solid mixture molar Gibbs energy departure
DGVPC	$\mu_i^{*,v}(p) - \mu_i^{*,v}(p_i^*)$	Vapor pure component molar Gibbs energy departure pressure correction
DGLPC	$\mu_i^{*,l}(p) - \mu_i^{*,l}(p_i^*)$	Liquid pure component molar Gibbs energy departure pressure correction
DGSPC	$\mu_i^{*,s}(p) - \mu_i^{*,s}(p_i^*)$	Solid pure component molar Gibbs energy departure pressure correction
DSV	$S_i^{*,v} - S_i^{*,ig}$	Vapor pure component molar entropy departure
DSL	$S_i^{*,l} - S_i^{*,ig}$	Liquid pure component molar entropy departure
DSS	$S_i^{*,s} - S_i^{*,ig}$	Solid pure component molar entropy departure
DSVMX	$S_m^v - S_m^{ig}$	Vapor mixture molar entropy departure
DSLMX	$S_m^l - S_m^{ig}$	Liquid mixture molar entropy departure

Property Name	Symbol	Description
DSSMX	$S_m^s - S_m^{ig}$	Solid mixture molar entropy departure
HNRY	H_{iA}	Henry's constant of supercritical component i in subcritical component A
HLXS	$H_m^{E,l}$	Liquid mixture molar excess enthalpy
HSXS	$H_m^{E,s}$	Solid mixture molar excess enthalpy
GLXS	$G_m^{E,l}$	Liquid mixture molar excess Gibbs energy
GSXS	$G_m^{E,s}$	Solid mixture molar excess Gibbs energy
PHILPC	$\theta^{*,l}$	Pure component liquid fugacity coefficient pressure correction
PHISPC	$\theta^{*,s}$	Pure component solid fugacity coefficient pressure correction
GAMPC	θ^{E}	Liquid activity coefficient pressure correction, symmetric convention
GAMPC1	θ^{*E}	Liquid activity coefficient pressure correction, asymmetric convention
HNRYPC	θ_{iA}^{∞}	Henry's constant pressure correction for supercritical component i in subcritical component A
XTRUE	x^t	True composition
MUVLP	$\eta_i^{*,v}(p=0)$	Pure component low pressure vapor viscosity
MUVPC	$\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0)$	Pure component vapor viscosity pressure correction
MUVMXLP	$\eta^v(p=0)$	Low pressure vapor mixture viscosity
MUVMXPC	$\eta^v(p) - \eta^v(p=0)$	Vapor mixture viscosity pressure correction
KVLP	$\lambda_i^{*,v}(p=0)$	Pure component low pressure vapor thermal conductivity
KVLP	$\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p=0)$	Pure component vapor thermal conductivity pressure correction
KVMXLP	$\lambda^v(p=0)$	Low pressure, vapor mixture thermal conductivity
KVMXPC	$\lambda^v(p) - \lambda^v(p=0)$	Vapor mixture thermal conductivity pressure correction

Intermediate Properties in the Aspen Physical Property System

Property Name	Symbol	Description
GAMMA	γ	Liquid phase activity coefficient
GAMUS	γ^*	Liquid phase activity coefficient, unsymmetric convention
GAMMAS	γ^s	Solid phase activity coefficient
WHNRY	w	Henry's constant mixing rule weighting factor
PL	$p_i^{*,l}$	Liquid pure component vapor pressure
PS	$p_i^{*,s}$	Solid pure component vapor pressure
DHVL	$\Delta_{vap}H_i^*$	Pure component enthalpy of vaporization
DHLS	$\Delta_{fus}H_i^*$	Pure component enthalpy of fusion
DHVS	$\Delta_{sub}H_i^*$	Pure component enthalpy of sublimation
VLPM	V_i^l	Partial molar liquid volume

Methods

This section describes the methods available for calculating the major and subordinate properties in the Aspen Physical Property System.

A method is an equation used to calculate physical properties based on universal scientific principles only, such as thermodynamics. This equation may contain assumptions, such as the vapor can be treated as ideal gas or the pressure is low enough to neglect the pressure correction. The equation may need properties and state variables but not correlation parameters to calculate a specific property.

Applied thermodynamics indicate that there usually is more than one method for calculating a particular property. For example, the enthalpy departure of a component in the liquid phase, $H_i^{*,l}$- $H_i^{*,ig}$ can be calculated from its fugacity coefficient in the liquid phase:

$$H_i^{*,l} - H_i^{*,ig} = -RT^2 \frac{\partial \ln \varphi_i^{*,l}}{\partial T}$$

This method is often used for supercritical solutes in liquid solution. Alternatively, the liquid departure function can be calculated from the vapor enthalpy departure and the heat of vaporization:

$$H_i^{*,l} - H_i^{*,ig} = H_i^{*,\nu} - H_i^{*,ig} - \Delta_{vap} H_i$$

Both methods are equally valid. There is another possibility, which is to calculate the departure function directly by an equation of state. Equations of state use correlation parameters and are therefore classified as models, so:

$$H_i^{*,l} - H_i^{*,ig} = f\left(p,\, T,\, \mathbf{correlation\,parameters}\right)$$

This is not a method but rather a valid alternative to calculate the enthalpy departure. To make the model available to the list of methods, a simple method is used that refers to a model:

$$H_i^{*,l} - H_i^{*,ig} = f\left(p,\, T,\, \mathbf{specified\ \ model}\right)$$

In general, a list of methods available for a property will be similar to the list presented here for the enthalpy departure. Compare these tables:

Vapor Fugacity Coefficient Methods	Vapor Entropy Methods
Liquid Fugacity Coefficient Methods	Liquid Entropy Methods
Solid Fugacity Coefficient Methods	Solid Entropy Methods
Vapor Enthalpy Methods	Molar Volume Methods
Liquid Enthalpy Methods	Viscosity Methods
Solid Enthalpy Methods	Thermal Conductivity Methods
Vapor Gibbs Energy Methods	Diffusion Coefficient Methods
Liquid Gibbs Energy Methods	Surface Tension Methods
Solid Gibbs Energy Methods	

In a method you can have any number of major properties, subordinate properties, or models. Usually there is a method that can be used with an equation of state approach and an alternative that is used with the activity coefficient approach (see Thermodynamic Property Methods in Overview of Aspen Physical Property Methods). There is always a method that refers to a model. Although there are a limited number of thermodynamic methods, in general, all the existing thermodynamic methods for each property are present.

Transport property methods are not as universal as thermodynamic methods. Therefore the transport property methods offered in the Aspen Physical Property System might not be exhaustive, but multiple methods for one property also exist.

All physical property methods available for calculating major and subordinate properties in the Aspen Physical Property System are provided in the physical property methods tables listed above. For each major or subordinate property, these tables list:

- Property symbol and name
- Property type: major or subordinate
- Methods available for calculating the property

For each method the fundamental equation is given. The table also lists which information is needed to specify each step in the method (see Routes and Models).

Example: Methods for calculating liquid mixture enthalpy

From the table labeled Liquid Enthalpy Methods, there are four methods for calculating HLMX:

Method 1 HLMX is calculated directly by an empirical model. The model may depend on temperature *T*, pressure *p*, liquid composition, and certain model specific parameters.

$$H^l = f^l\left(T,\, p,\, x_i,\, parameters\right)$$

Method 2 HLMX is calculated from the ideal liquid mixture enthalpy and excess enthalpy.

$$H_m^l = \sum x_i H_i^{*,l} + H_m^{E,l}$$

$$(HLMX = \sum x_i HL_i + HLXS)$$

The major property HLMX depends on the liquid pure component enthalpy, HL, and the liquid mixture excess enthalpy, HLXS. HL is also a major property, while HLXS is a subordinate property.

Method 3 HLMX is calculated from the ideal gas mixture enthalpy, HIGMX, and the liquid mixture enthalpy departure, DHLMX.

$$H_m^l = H_m^{ig} + \left(H_m^l - H_m^{ig}\right)$$

(HLMX = HIGMX + DHLMX)

The subordinate property DHLMX can be calculated by one of the methods listed in the table labeled Liquid Enthalpy Methods. In all the equation of state property methods, DHLMX is calculated directly by an equation of state (that is, method 1 is used for DHLMX).

Method 4 HLMX is calculated directly by the Electrolyte model.

$$H_m^l = f\left(x^t\right)$$

Where:

x^t = The component true mole fractions

(x^t is also the symbol for the subordinate property XTRUE:
HLMX = f (XTRUE)).

Vapor Fugacity Coefficient Methods

Vapor Pure Component Fugacity Coefficient

$\varphi_i^{*,v}$, PHIV, major property

Method Code	Method	Route Structure Information Required
1	Directly by a model, such as an equation- of-state model.	$\varphi_i^{*,v}$ Model name

Vapor Fugacity Coefficient of a Component in a Mixture

φ_i^v, PHIVMX, major property

Method Code	Method	Route Structure Information Required
1	Directly by a model, such as an equation-of-state mode	φ_i^v Model name (Default: φ_i^v=1)
2	From vapor pure component fugacity coefficients $\varphi_i^v=f(y_i, \varphi_i^{*,v})$	$\varphi_i^{*,v}$ Route ID φ_i^v Model name
3	Directly by an equation-of-state model that uses advanced mixing rules that employs γ_i from a gamma model (for example, MHV2, Wong-Sandler) $\varphi_i^v=f(\gamma_i)$	γ_i Model name φ_i^v Model name

Liquid Fugacity Coefficient Methods

Liquid Pure Component Fugacity Coefficient

$\varphi_i^{*,l}$, PHIL, major property

Method Code	Method	Route Structure Information Required
1	Directly by a model, such as an equation-of-state model	$\varphi_i^{*,l}$ Model name
2	From vapor pressure, vapor fugacity coefficient and Poynting correction $\dfrac{\varphi_i^{*,v}\left(T,p_i^{*,l}\right)p_i^{*,l}\theta_i^{*,l}}{p}$	$p^{*,l}$ Model name $\varphi_i^{*,v}$ Model name (Default: $\varphi_i^{*,v} = 1$) $\theta^{*,l}$ Route ID (Default: $\theta^{*,l} = 1$)
3	By a model for supercritical components; from vapor pressure, vapor fugacity coefficient and Poynting correction for subcritical components For subcritical components: $\varphi_i^{*,v}\left(T,p_i^{*,l}\right)\frac{p_i^{*,l}}{p}\exp\left(\frac{1}{RT}\int_{p_i^{*,l}}^{p}V^{*,l}dp\right)$	$\varphi_i^{*,l}$ Model name $p^{*,l}$ Model name $\varphi_i^{*,l}$ Model name $V_i^{*,l}$ Model name
4	Steam table for water, otherwise from $\dfrac{\varphi_i^{*,v}\left(T,p_i^{*,l}\right)p_i^{*,l}\theta_i^{*,l}}{p}$	$p^{*,l}$ Model name $\varphi_i^{*,v}$ Model name (Default: $\varphi_i^{*,v} = 1$) $\theta^{*,l}$ Route ID (Default: $\theta^{*,l} = 1$)

Liquid Pure Component Fugacity Coefficient Pressure Correction

$\theta_i^{*,l}$, PHILPC, subordinate property

Method Code	Method	Route Structure Information Required
1	Poynting correction calculated from integration of liquid molar volume $\exp\left(\frac{1}{RT}\int_{p_i^{*,l}}^{p}V^{*,l}dp\right)$	$p^{*,l}$ Model name $V_i^{*,l}$Model name
2	Poynting correction calculated by a model	$\theta_i^{*,l}$ Model name

Liquid Fugacity Coefficient of Component in a Mixture

φ_i^l, PHILMX, major property

Method Code	Method	Route Structure Information Required
1	Directly by a model, such as an equation-of-state model. This method is used in all equation-of-state property methods.	φ_i^l Model name
2	By the gamma-phi approach using activity coefficient model and reference state fugacity coefficient including Poynting correction $\gamma_i\varphi_i^{*,l}\theta_i^E$	γ_i Model name (Default: $\gamma_i = 1$) $\varphi_i^{*,l}$ Route ID θ_i^E Route ID (Default: $\theta_i^E = 1$)
3	By the gamma-phi approach with Henry's law used for super-critical components (unsymmetric convention) For subcritical components (A or B): $\varphi_A^l=\delta_A\gamma_A\varphi_A^{*,l}$ For supercritical components (i or j) $\varphi_i^l = \gamma_i \left(\frac{H_i}{p\gamma_i^\infty}\right)$ Where: $\ln\delta_A = \frac{w_A}{x_A}\sum_j x_j\left[\ln\left(\frac{H_{iA}}{\gamma_{jA}^\infty}\right) - \ln\left(\frac{H_j}{\gamma_j^\infty}\right)\right]$ (or $\delta_A = 1$) $\ln\left(\frac{H_i}{\gamma_i^\infty}\right) = \sum_B w_B \ln\left(\frac{H_{iB}}{\gamma_{iB}^\infty}\right)$ $\ln\gamma_i^\infty = \lim_{\sum_j x_j\to 0}(\ln\gamma_i)$ $\sum_B w_B = 1$	Subcritical: $\varphi_A^{*,l}$ Route ID γ_A Model name (Default: $\gamma_A = 1$) Supercritical: H_{jA} Route ID w_A Model option code w_B Model name w_B Model option code Method Option code † 0: Do not calculate H_i 1: Calculate H_i (Default = 0)
4	By the gamma-phi approach with true components calculations. Should be used with electrolytes systems. $\gamma_i\varphi_i^{*,l}\theta_i^E$ Where: $\gamma_i = f(x^t)$	γ_i Model name (Default: $\gamma_i = 1$) $\varphi_i^{*,l}$ Route ID θ_i^E Route ID (Default: $\theta_i^E = 1$) x^t Route ID

Method Code	Method	Route Structure Information Required
5	By the gamma-phi approach with true components and Henry's law (unsymmetric convention). Should be used with electrolytes systems. For subcritical components (A or B): $\varphi_A^l = \delta_A \gamma_A \varphi_A^{*,l}$ Where: $\gamma_A = f\left(x^t\right)$ For supercritical components (i or j) $\varphi_i^l = \gamma_i \left(\frac{H_i}{p\gamma_i^\infty}\right)$ Where: $\ln \delta_A = \frac{W_A}{X_A} \sum_j x_j \left[\ln\left(\frac{H_{iA}}{\gamma_{jA}^\infty}\right) - \ln\left(\frac{H_j}{\gamma_j^\infty}\right)\right]$ (or $\delta_A = 1$) $\ln\left(\frac{H_i}{\gamma_i^\infty}\right) = \sum_B w_B \ln\left(\frac{H_{iB}}{\gamma_{iB}^\infty}\right)$ $\ln \gamma_i^\infty = \lim_{\sum_j x_j \to 0} \left(\ln \gamma_i\right)$ $\sum_B w_B = 1$	Subcritical: $\varphi_i^{*,l}$ Route ID γ_A Model name (Default: $\gamma_A = 1$) x^t Route ID Supercritical: H_{jA} Route ID w_A Model option code w_B Model name w_B Model option code Method Option code † 0: Do not calculate H_i 1: Calculate H_i (Default = 0)
6	Directly by an equation-of-state model that uses advanced mixing rules, employing gE from a gamma model (for example, MHV2, Wong-Sandler) $\varphi_i^l = f(\gamma_i)$	γ_i Model name φ_i^l Model name
7	Similar to method 3, but the fugacity coefficients of some components can be overridden by a special PHILMX model. Currently, this method is used to override the fugacity coefficients of CO_2, H_2S, NH_3, and H_2O calculated by an activity coefficient property method by the API sour water model.	

True Composition Computed from Apparent Composition and Electrolyte Chemistry

x^t, XTRUE, subordinate property

Method Code	Method	Route Structure Information Required
1	From solution chemistry and activity coefficients $x^t = f\left(T,\, x_i,\, \gamma_i,\, \text{Chemistry}\right)$	γ_i Model name

Liquid Activity Coefficient Pressure Correction

θ_i^E, GAMPC, subordinate property

Method Code	Method	Route Structure Information Required
1	From integration of partial molar volume $\exp\left(\frac{1}{RT}\int_{p^{ref}}^{p}\left(V_i^l - V_i^{*,l}\right)dp\right)$	V_i^l Model name $V_i^{*,l}$Model name
2	Directly by a model	θ_i^E Model name

Liquid Activity Coefficient Pressure Correction

θ_i^E, GAMPC1, subordinate property

Method Code	Method	Route Structure Information Required
1	From integration of partial molar volume $\exp\left(\frac{1}{RT}\int_{p^{ref}}^{p} V_i^l dp\right)$	V_i^l Model name
2	Directly by a model	$\theta_i^{*,E}$ Model name

Henry's Constant

H_{iA}, HNRY, subordinate property

Method Code	Method	Route Structure Information Required
1	Directly by a model, such as a TABPOLY model	H_{iA} Model name
2	From Henry's constant correlation $H_{iA}\left(p^{ref}, T\right)\theta_{iA}^{\infty}$	H_{iA} Model name θ_{iA}^{∞} Route ID (Default: θ_{iA}^{∞} = 1) p^{ref} defined by the p^{ref} option code of HNRYPC

Henry's Constant Pressure Correction

θ_{iA}^{∞}, HNRYPC, subordinate property

Method Code	Method	Route Structure Information Required
1	From integration of partial molar volume $\exp\left(\frac{1}{RT}\int_{p^{ref}}^{p} V_i^l \, dp\right)$	$p_A^{*,l}$ Model name (if needed for p^{ref} V_i^{∞} Model name
2	Directly by a model	θ_{iA}^{∞} Model name

† For calculating fugacity coefficients, H_i is not needed explicitly; the quantity needed is H_i/γ_i^{∞}. Methods which can calculate this quantity directly have an option code to force the calculation of H_i. This can be set to 1 when H_i is needed for Property Set property reporting. Certain property methods need H_i for other reasons and these methods set this option code to 1.

Solid Fugacity Coefficient Methods

Solid Pure Component Fugacity Coefficient

$\varphi_i^{*,s}$, PHIS, major property

Method Code	Method	Route Structure Information Required
1	Specified Model	$\varphi_i^{*,s}$ Model name

Method Code	Method	Route Structure Information Required
2	$\varphi_i^{*,v}\left(T, p_i^{*,s}\right) p_i^{*,s} \frac{\theta_i^{*,s}}{p}$	$p_i^{*,s}$ Model name $\varphi_i^{*,v}$ Model name (Default: $\varphi_i^{*,v} = 1$) $\theta_i^{*,s}$ Route ID (Default: $\theta_i^{*,s} = 1$)
3	$\varphi_i^{*,s}\varphi_i^{*,l}$	$\varphi_i^{*,s}$ Model name $\varphi_i^{*,l}$ Route ID

Solid Pure Component Fugacity Coefficient Pressure Correction

$\theta_i^{*,s}$, PHISPC, subordinate property

Method Code	Method	Route Structure Information Required
1	From integration of solid molar volume $\exp\left(\frac{1}{RT}\int_{p^{*,s}}^{p} V_i^{*,s}\, dp\right)$	$p_i^{*,s}$ Model name $V_i^{*,s}$ Model name
2	Directly by a model	$\theta_i^{*,s}$ Model name

Solid Fugacity Coefficient of a Component in a Mixture

φ_i^s, PHISMX, major property

Method Code	Method	Route Structure Information Required
1	Directly by a model	φ_i^s Model name
2	From solid pure component fugacity coefficients $\varphi_i^s = f(x_i^s, \varphi_i^{*,s})$	$\varphi_i^{*,s}$ Route ID φ_i^s Model name
3	From solid activity coefficient and pure component fugacity coefficient $\gamma_i^s\varphi_i^{*,s}$	γ_i^s Model name $\varphi_i^{*,s}$ Route ID

Vapor Enthalpy Methods

Vapor Pure Component Molar Enthalpy

$H_i^{*,v}$, HV, major property

Method Code	Method	Route Structure Information Required
1	Directly by a model	$H_i^{*,v}$ Model name
2	From ideal gas enthalpy and vapor enthalpy departure $H_i^{*,ig} + \left(H_i^{*,\nu} - H_i^{*,ig}\right)$	$(H_i^{*,v} - H_i^{*,ig})$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig}=0$)
3	From liquid pure component molar enthalpy and heat of vaporization $H_i^{*,l} + \Delta_{vap}H_i^*$	$H_i^{*,l}$ Route ID $\Delta_{vap}H_i^*$ Model name

Vapor Pure Component Molar Enthalpy Departure

$H_i^{*,v} - H_i^{*,ig}$, DHV, subordinate property

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(H_i^{*,v} - H_i^{*,ig})$ Model name
2	From temperature derivative of vapor pure component fugacity coefficient $-RT^2\left(\frac{\partial \ln \varphi_i^{*,v}}{\partial T}\right)$	$\varphi_i^{*,v}$ Model name

Vapor Mixture Molar Enthalpy

H_m^v, HVMX, major property

Method Code	Method	Route Structure Information Required
1	Directly by a model	H_m^v Model name

Method Code	Method	Route Structure Information Required
2	As mole-fraction average of pure component molar enthalpy $$\sum_i y_i H_i^{*,\nu}$$	$H_i^{*,v}$ Route ID
3	From ideal gas enthalpy and vapor enthalpy departure $H_m^{ig} + (H_m^v - H_m^{ig})$	$(H_m^v - H_m^{ig})$ Route ID (Default: $H_m^v - H_m^{ig}=0$)
4	Directly by a model that uses mixing rules based on vapor pure component molar enthalpy $H_i^{*,v}$	$H_i^{*,v}$ Route ID H_m^v Model name used to provide mixing rules for the pure component property $H_i^{*,v}$

Vapor Mixture Molar Enthalpy Departure

$H_m^v - H_m^{ig}$, DHVMX, subordinate property

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(H_m^v - H_m^{ig})$ Model name
2	From temperature derivative of vapor pure component fugacity coefficient $$-RT^2 \sum_i y_i \left(\frac{\partial \ln \varphi_i^v}{\partial T} \right)$$	φ_i^v Model name
3	directly by an equation-of-state model that uses advanced mixing rules that employs γ_i from a gamma model (e.g., MHV2, Wong-Sandler) $H_m^v - H_m^{ig} = f(\gamma_i)$	γ_i Model name Equation of state model name

Liquid Enthalpy Methods

Liquid Pure Component Molar Enthalpy

$H_i^{*,l}$, HL, major property

Method Code	Method	Route Structure Information Required
1	Directly by a model	$H_i^{*,l}$ Model name
2	From ideal gas pure component molar enthalpy and the liquid enthalpy departure $H_i^{*,ig} + (H_i^{*,l} - H_i^{*,ig})$	$(H_i^{*,l} - H_i^{*,ig})$ Route ID

Liquid Pure Component Molar Enthalpy Departure

$H_i^{*,l} - H_i^{*,ig}$, DHL, subordinate property

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(H_i^{*,l} - H_i^{*,ig})$ Model name
2	From temperature derivative of liquid pure component fugacity coefficient $-RT^2\left(\frac{\partial \ln \varphi_i^{*,l}}{\partial T}\right)$	$\varphi_i^{*,l}$ Model name
3	From vapor enthalpy departure, enthalpy of vaporization, and liquid phase pressure correction, used in activity coefficient methods $(H_i^{*,v}(T, p_i^{*,l}) - H_i^{*,ig}(T))$ $- \Delta_{vap}H_i^{*}(T)$ $+ (H_i^{*,l}(T, p) - H_i^{*,l}(T, p_i^{*,l}))$	p_i^l Model name $(H_i^{*,v} - H_i^{*,ig})$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) $\Delta_{vap}H_i^l$ Model name $(H_i^{*,l}(T, p) - H_i^{*,l}(T, p_i^{*,l}))$ Route ID (Default: $(H_i^{*,l}(T, p) - H_i^{*,l}(T, p_i^{*,l})) = 0$)
4	Same as method 3, but for a polymer property method	p_i^l Model name $(H_i^{*,v} - H_i^{*,ig})$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) $\Delta_{vap}H_i^l$ Model name $(H_i^{*,l}(T, p) - H_i^{*,l}(T, p_i^{*,l}))$ Route ID (Default: $(H_i^{*,l}(T, p) - H_i^{*,l}(T, p_i^{*,l})) = 0$)

Method Code	Method	Route Structure Information Required
5	Same as method 3, but for an electrolyte activity coefficient property method	p_i^l Model name $(H_i^{*,v} - H_i^{*,ig})$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) $\Delta_{vap}H_i^l$ Model name $(H_i^{*,l}(T, p) - H_i^{*,l}(T, p_i^{*,l}))$ Route ID (Default: $(H_i^{*,l}(T, p) - H_i^{*,l}(T, p_i^{*,l})) = 0$)

Liquid Pure Component Molar Enthalpy Departure Pressure Correction

$(H_i^{*,l}(T, p) - H_i^{*,l}(T, p_i^{*,l}))$, DHLPC, subordinate property

Method Code	Method	Route Structure Information Required
1	From the difference between liquid enthalpy departure at the system pressure and at the vapor pressure $(H_i^{*,l}(T, p) - H_i^{*,ig}(T)) - (H_i^{*,l}(T, p_i^{*,l}) - H_i^{*,ig}(T))$	$p_i^{*,l}$ Model name $(H_i^{*,l} - H_i^{*,ig})$ Route ID
2	From integration of liquid molar volume and its temperature derivative $\int_{p_i}^{p} \left[V_i^{*,l} - T \left(\frac{\partial V_i^{*,l}}{\partial T} \right)_p \right] dp$	$p_i^{*,l}$ Model name $V_i^{*,l}$ Model name Integration option code (Default: 1 point)
3	Directly by a model	$\left(H_i^{*,l}(T, p) - H_i^{*,l}\left(T, p_i^{*,l}\right) \right)$ Model name

Liquid Mixture Molar Enthalpy

H_m^l, HLMX, major property

Method Code	Method	Route Structure Information Required
1	Directly by a model	H_m^l Model name
2	As mole-fraction average of liquid pure component molar enthalpy and enthalpy of mixing (excess molar enthalpy) $\sum_i x_i H_i^{*,l} + H_m^{E,l}$	$H_i^{*,l}$ Route ID $H_i^{E,l}$ Route ID (Default: $H_i^{E,l}$ =0)
3	From ideal gas enthalpy and liquid enthalpy departure $H_m^{ig} + (H_m^l - H_m^{ig})$	$(H_m^l - H_m^{ig})$ Route ID
4	By an electrolyte model (x^t)	H_m^l Model name x^t Route ID
5	Directly by a model using mixing rules based on liquid pure component molar enthalpy $H_i^{*,l}$	$H_i^{*,l}$ Route ID H_m^l Model name used to provide mixing rules for the pure component property $H_i^{*,l}$
6	From ideal gas enthalpy and liquid enthalpy departure for an electrolyte system $H_m^{ig} + (H_m^l - H_m^{ig})$	$(H_m^l - H_m^{ig})$ Route ID

Liquid Mixture Molar Enthalpy Departure

$H_m^l - H_m^{ig}$, DHLMX, subordinate property

Method Code	Method	Route Structure Information Required
1	Directly by a model, such as an equation-of-state model	$(H_m^l - H_m^{ig})$ Model name
2	From mole-fraction average of pure component enthalpy departure and enthalpy of mixing (excess enthalpy) $\sum_i x_i \left(H_i^{*,l} - H_i^{*,ig}\right) + H_m^{E,l}$	$(H_i^{*,l} - H_i^{*,ig})$ Route ID $H_m^{E,l}$ Route ID (Default: $H_m^{E,l}$ = 0)

Method Code	Method	Route Structure Information Required
3	From temperature derivative of fugacity coefficient for supercritical components; pure component enthalpy departure for subcritical components (unsymmetric convention) For subcritical components A or B: $\sum_i x_A \left(H_A^{*,l} - H_A^{*,ig}\right) + H_m^{E,l}$ $H_m^{E,l} = -RT^2 \sum_B x_B \left(\frac{\partial \ln \gamma_B}{\partial T}\right)$	$(H_A{}^{*,l}$ - $H_A{}^{*,ig})$ Route ID where: γ_B Model name
	For supercritical component i or j: $-RT^2 \sum_j x_j \left(\frac{\partial \ln \varphi_j^l}{\partial T}\right)$	H_{iB} Route ID
	where: $\varphi_\iota^I = \gamma_i \left(\frac{H_i}{p\gamma_i^\infty}\right)$ $\ln\left(\frac{H_i}{\gamma_i^\infty}\right) = \sum_B w_B \ln\left(\frac{H_{iB}}{\gamma_{iB}^\infty}\right)$ $\ln \gamma_i^\infty = \lim_{\sum_j x_j \to 0} (\ln \gamma_i)$ $\sum_B w_B = 1$	w_B Model name w_B Model option code
4	Special mixing rule for Aspen Polymers $\sum_i x_i \left(H_i^{*,l} - H_i^{*,ig}\right) -$ $RT^2 \sum_i x_i \left(\frac{M_i}{M_i^t}\right) \left(\frac{\partial \ln \gamma_i}{\partial T}\right)$	M_i Reference mole weight (from parameter MW) M_i^t True number-average mole weight γ_i Model name Equation of state model name

Method Code	Method	Route Structure Information Required
5	Unsymmetric convention for Aspen Polymers For subcritical components A or B: $\sum_i x_A \left(H_A^{*,l} - H_A^{*,ig}\right) + H_m^{E,l}$ $H_m^{E,l} = -RT^2 \sum_B x_B \left(\frac{M_i}{M_i^t}\right) \left(\frac{\partial \ln \gamma_B}{\partial T}\right)$ For supercritical component i or j: $-RT^2 \sum_j x_j \left(\frac{\partial \ln \varphi_j^l}{\partial T}\right)$ where: $\varphi_\iota^I = \gamma_i \left(\frac{H_i}{p\gamma_i^\infty}\right)$ $\ln\left(\frac{H_i}{\gamma_i^\infty}\right) = \sum_B w_B \ln\left(\frac{H_{iB}}{\gamma_{iB}^\infty}\right)$ $\ln \gamma_i^\infty = \lim_{\sum_j x_j \to 0} (\ln \gamma_i)$ $\sum_B w_B = 1$	$(H_A^{*,l}$ - $H_A^{*,ig})$ Route ID where: γ_B Model name M_i Reference mole weight (from parameter MW) M_i^t True number-average mole weight H_{iB} Route ID w_B Model name w_B Model option code
6	Unsymmetric convention, as in method 3 but for electrolyte activity coefficient property method	$(H_A^{*,l}$ - $H_A^{*,ig})$ Route ID γ_B Model name H_{iB} Route ID w_B Model name w_B Model option code
7	Calculated from liquid fugacity coefficient using electrolyte models GMENRTLQ & GMENRTLS	See ENRTL-RK or ENRTL-SR

Liquid Mixture Molar Excess Enthalpy

$H_m^{E,l}$, HLXS, subordinate property

Method Code	Method	Route Structure Information Required
1	Directly by a model	$H_m^{E,l}$ Model name
2	From the temperature derivative of activity coefficient $H_m^{E,l} = -RT^2 \sum_i x_i \left(\frac{\partial \ln \gamma_i}{\partial T} \right)$	γ_i Model name
3	Method for Aspen Polymers only: $H_m^{E,l} = -RT^2 \sum_i x_i \left(\frac{M_i}{M_i^t} \right) \left(\frac{\partial \ln \gamma_i}{\partial T} \right)$	γ_i Model name M_i Reference mole weight (from parameter MW) M_i^t True number-average mole weight

Solid Enthalpy Methods

Solid Pure Component Molar Enthalpy

$H_i^{*,s}$ HS (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$H_i^{*,s}$ Model name
2	From ideal gas enthalpy and solid enthalpy departure $H_i^{*,ig} + (H_i^{*,s} - H_i^{*,ig})$	$(H_i^{*,s} - H_i^{*,ig})$ Route ID

Solid Pure Component Molar Enthalpy Departure

$H_i^{*,s} - H_i^{*,ig}$ DHS (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(H_i^{*,s} - H_i^{*,ig})$ Model name
2	From vapor enthalpy departure and heat of sublimation $(H_i^{*,v}(T,p_i^{*,s}) - H_i^{*,ig}(T))$ $- \Delta_{sub}H_i^{*}(T)$ $+ (H_i^{*,s}(T,p) - H_i^{*,s}(T,p_i^{*,s}))$	$p_i^{*,s}$ Model name $(H_i^{*,v} - H_i^{*,ig})$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) $\Delta_{sub}H_i^{*}(T)$ Model name $(H_i^{*,s}(T,p) - H_i^{*,s}(T,p_i^{*,s}))$ Route ID (Default: $H_i^{*,s}(T,p) - H_i^{*,s}(T,p_i^{*,s}) = 0$)

Solid Pure Component Enthalpy Departure Pressure Correction

$H_i^{*,s}(T,p) - H_i^{*,s}(T,p_i^{*,s})$ DHSPC (subordinate property)

Method Code	Method	Route Structure Information Required
1	From integration of solid molar volume and its temperature derivative $$\int_{p_i^{*,s}}^{p} \left[V_i^{*,s} - T \left(\frac{\partial V_i^{*,s}}{\partial T} \right)_p \right] dp$$	$p_i^{*,s}$ Model name $V_i^{*,s}$ Model name

Solid Mixture Molar Enthalpy

H_m^s HSMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	H_m^s Model name
2	As mole fraction average of solid pure component molar enthalpy and enthalpy of mixing (excess molar enthalpy) $$\sum_i x_i^s H_i^{*,s} + H_m^{E,s}$$	$H_i^{*,s}$ Route ID $H_m^{E,s}$ Route ID (Default: $H_m^{E,s} = 0$)
3	From ideal gas enthalpy and solid enthalpy departure $H_m^{ig} + (H_m^s - H_m^{ig})$	$(H_m^s - H_m^{ig})$ Route ID
4	From solid pure component molar enthalpy $H_i^{*,s}$ using a mixing rule	$H_i^{*,s}$ Route ID H_m^s Model name used to provide mixing rules for the pure component property $H_i^{*,s}$

Solid Mixture Molar Enthalpy Departure

$H_m^s - H_m^{ig}$ DHSMX (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	(H_m^s - H_m^{ig}) Model name
2	From mole-fraction average of pure component enthalpy departure and excess enthalpy $\sum_i x_i^s \left(H_i^{*,s} - H_i^{*,ig}\right) + H_m^{E,s}$	(H_i^s - H_i^{ig}) Route ID $H_m^{E,s}$ Route ID (Default: $H_m^{E,s}$ = 0)

Solid Mixture Molar Excess Enthalpy

$H_m^{E,s}$ HSXS (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$H_m^{E,s}$ Model name
2	From temperature derivative of activity coefficient $H_m^{E,s} = -RT^2 \sum_i x_i^s \left(\frac{\partial \ln \gamma_i^s}{\partial T}\right)$	γ_i Model name

Vapor Gibbs Energy Methods

Vapor Pure Component Molar Gibbs Free Energy

$\mu_i^{*,v}$ GV (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$\mu_i^{*,v}$ Model name
2	From ideal gas Gibbs free energy and vapor Gibbs free energy departure $\mu_i^{*,ig}$ + ($\mu_i^{*,v}$ - $\mu_i^{*,ig}$)	($\mu_i^{*,v}$ - $\mu_i^{*,ig}$) Route ID (Default: $\mu_i^{*,v}$ - $\mu_i^{*,ig}$= 0)

Vapor Pure Component Molar Gibbs Free Energy Departure

$\mu_i^{*,v}$ - $\mu_i^{*,ig}$ DGV (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	($\mu_i^{*,v}$ - $\mu_i^{*,ig}$) Model name
2	From vapor pure component fugacity coefficient $RT\ln\varphi_i^{*,v} + RT\ln\left(\frac{p}{p^{ref}}\right)$	$\varphi_i^{*,v}$ Route ID

Vapor Mixture Molar Gibbs Free Energy

G_m^v GVMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	G_m^vModel name
2	As mole-fraction average of vapor pure component Gibbs free energy $\sum_i y_i\mu_i^{*,v} + RT\sum_i y_i\ln y_i$	$\mu_i^{*,v}$ Route ID
3	From ideal gas Gibbs free energy and vapor Gibbs free energy departure G_m^{ig} + (G_m^v - G_m^{ig})	(G_m^v - G_m^{ig}) Route ID (Default: G_m^v - G_m^{ig}= 0)
4	From vapor pure component Gibbs free energy $\mu_i^{*,v}$ using a mixing rule	$\mu_i^{*,v}$ Route ID G_m^v Model name used to provide mixing rules for the pure component property $\mu_i^{*,v}$

Vapor Mixture Molar Gibbs Free Energy Departure

G_m^v - G_m^{ig} DGVMX (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	(G_m^v - G_m^{ig}) Model name
2	From vapor fugacity coefficient $RT\sum_i y_i\ln\varphi_i^v + RT\ln\left(\frac{p}{p^{ref}}\right)$	φ_i^v Route ID (Default: φ_i^v= 1)
3	Directly by an equation-of-state model that uses advanced mixing rules, using a gamma model G_m^v - G_m^{ig} = $f(\gamma_i)$	γ_i Model name Equation of state model name

Liquid Gibbs Energy Methods

Liquid Pure Component Molar Gibbs Free Energy

$\mu_i^{*,l}$ GL (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$\mu_i^{*,l}$ Model name
2	From ideal gas Gibbs free energy and liquid Gibbs free energy departure $\mu_i^{*,ig} + (\mu_i^{*,l} - \mu_i^{*,ig})$	$(\mu_i^{*,l} - \mu_i^{*,ig})$ Route ID

Liquid Pure Component Molar Gibbs Free Energy Departure

$\mu_i^{*,l} - \mu_i^{*,ig}$ DGL (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\mu_i^{*,l} - \mu_i^{*,ig})$ Model name
2	Liquid pure component fugacity coefficient $RT\ln\varphi^{*,l} + RT\ln\left(\frac{p}{p^{ref}}\right)$	$\varphi_i^{*,l}$ Route ID
3	From vapor Gibbs free energy departure and liquid Gibbs free energy departure pressure correction $(\mu_i^{*,l}(T,p_i^{*,l}) - \mu_i^{*,ig}(T))$ $+ (\mu_i^{*,l}(T,p) - \mu_i^{*,l}(T,p_i^{*,l}))$	$p_i^{*,l}$ Model name $(\mu_i^{*,l} - \mu_i^{*,ig})$ Route ID (Default: $\mu_i^{*,l} - \mu_i^{*,ig} = 0$) $(\mu_i^{*,l}(T,p) - \mu_i^{*,l}(T,p_i^{*,l}))$ Route ID (Default: $\mu_i^{*,l}(T,p) - \mu_i^{*,l}(T,p_i^{*,l}) = 0$)

Liquid Pure Component Molar Gibbs Free Energy Departure Pressure Correction

$\mu_i^{*,l}(T,p) - \mu_i^{*,l}(T,p_i^{*,l})$ DGLPC (subordinate property)

Method Code	Method	Route Structure Information Required
1	From the difference between Gibbs free energy departure at the system pressure and at the vapor pressure $(\mu_i^{*,l}(T,p) - \mu_i^{*,ig}(T))$ $- (\mu_i^{*,l}(T,p_i^{*,l}) - \mu_i^{*,ig}(T))$	$p_i^{*,l}$ Model name $(\mu_i^{*,l} - \mu_i^{*,ig})$ Route ID
2	By integration of liquid molar volume $$\int_{p_i^{*,l}}^{p} V_i^{*,l}\,dp$$	$p_i^{*,l}$ Model name $V_i^{*,l}$ Model Name

Liquid Mixture Molar Gibbs Free Energy

G_m^l GLMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	G_m^l Model name
2	As mole-fraction average of vapor pure component Gibbs free energy and excess Gibbs free energy $$\sum_i x_i \mu_i^{*,l} + RT \sum_i x_i \ln x_i + G_m^{E,l}$$	$\mu_i^{*,l}$ Route ID $G_m^{E,l}$ Route ID (Default: $G_m^{E,l} = 0$)
3	From ideal gas Gibbs free energy and liquid Gibbs free energy departure $G_m^{ig} + (G_m^l - G_m^{ig})$	
4	By an electrolyte model (x^t)	Model name x^t Route ID

Method Code	Method	Route Structure Information Required
5	From liquid pure component Gibbs free energy departure, liquid excess Gibbs free energy, and polymer properties $\sum_i x_i \left(\mu_i^{*,l} - \mu_i^{*,ig}\right) + G_m^{E,l}$ $+\sum_i x_i \frac{MW_i}{TMW_i} \ln\left(\frac{MW_i}{TMW_i}\frac{x_i}{\sum_k \frac{x_k MW_k}{TMW_k}}\right)$ Where TMW is the true molecular weight for polymers.	$\mu_i^{*,l}$ Route ID $G_m^{E,l}$ Route ID (Default: $G_m^{E,l} = 0$)
6	From liquid pure component Gibbs free energy $\mu_i^{*,l}$ using mixing rules	$\mu_i^{*,l}$ Route ID G_m^l Model name used to provide mixing rules for the pure component property $\mu_i^{*,l}$
7	From ideal gas Gibbs free energy and liquid Gibbs free energy departure for an electrolyte system $G_m^{ig} + (G_m^l - G_m^{ig})$	

Liquid Mixture Molar Gibbs Free Energy Departure

$G_m^l - G_m^{ig}$ DGLMX (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(G_m^l - G_m^{ig})$ Model name
2	From mole-fraction average of pure component Gibbs free energy departure and excess Gibbs free energy $\sum_i x_i \left(\mu_i^{*,l} - \mu_i^{*,ig}\right) + G_m^{E,l}$	$(\mu_i^{*,l} - \mu_i^{*,ig})$ Route ID $G_m^{E,l}$ Route ID (Default: $G_m^{E,l} = 0$)
3	From liquid fugacity coefficient $RT \sum_i x_i \ln \varphi_i^l + RT \ln\left(\frac{p}{p^{ref}}\right)$	φ_i^l Route ID

Method Code	Method	Route Structure Information Required
4	Directly by an equation-of-state model that uses advanced mixing rules, using a gamma model $G_m^l - G_m^{ig} = f(\gamma_i)$	γ_i Model name Equation of state model name
5	From liquid fugacity coefficient using electrolyte activity coefficient model $RT\sum_i x_i \ln\varphi_i^l + RT\ln\left(\frac{p}{p^{ref}}\right)$	φ_i^l Route ID

Liquid Mixture Molar Excess Gibbs Free Energy

$G_m^{E,l}$ GLXS (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$G_m^{E,l}$ Model name
2	From activity coefficients $RT\sum_i x_i \ln\gamma_i$	γ_i Model name
3	From polymer properties $RT\sum_i x_i \frac{MW_i}{TMW_i}\left[\ln\gamma_i + \ln\frac{TMW_i}{MW_i}\left(\sum_k x_k \frac{MW_k}{TMW_k}\right)\right]$ Where TMW is the true molecular weight for polymers.	γ_i Model name

Solid Gibbs Energy Methods

Solid Pure Component Molar Gibbs Free Energy

$\mu_i^{*,s}$ GS (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$\mu_i^{*,s}$ Model name
2	From ideal gas Gibbs free energy and solid Gibbs free energy departure $\mu_i^{*,ig} + (\mu_i^{*,s} - \mu_i^{*,ig})$	$(\mu_i^{*,s} - \mu_i^{*,ig})$ Route ID

Solid Pure Component Molar Gibbs Free Energy Departure

$\mu_i^{*,s} - \mu_i^{*,ig}$ DGS (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\mu_i^{*,s} - \mu_i^{*,ig})$ Model name
2	From solid pure component fugacity coefficient $RT \ln \varphi^{*,s} + RT \ln\left(\frac{p}{p^{ref}}\right)$	$\varphi_i^{*,s}$ Route ID
3	From vapor pure component Gibbs free energy departure $(\mu_i^{*,s}(T,p_i^{*,s}) - \mu_i^{*,ig}(T))$ $+ (\mu_i^{*,s}(T,p) - \mu_i^{*,s}(T,p_i^{*,s}))$	$p_i^{*,s}$ Model name $(\mu_i^{*,s}(T,p_i^{*,s}) - \mu_i^{*,ig}(T))$Route ID (Default: $(\mu_i^{*,s}(T,p_i^{*,s}) - \mu_i^{*,ig}(T)) = 0$) $(\mu_i^{*,s}(T,p) - \mu_i^{*,s}(T,p_i^{*,s}))$ Route ID (Default: $(\mu_i^{*,s}(T,p) - \mu_i^{*,s}(T,p_i^{*,s})) = 0$)

Solid Pure Component Molar Gibbs Free Energy Departure Pressure Correction

$\mu_i^{*,s}(T,p) - \mu_i^{*,s}(T,p_i^{*,s})$ DGSPC (subordinate property)

Method Code	Method	Route Structure Information Required
1	From integration of solid molar volume $\int_{p_i^{*,l}}^{p} V_i^{*,l}\,dp$	$p_i^{*,l}$ Model name $V_i^{*,l}$ Model Name

Solid Mixture Molar Gibbs Free Energy

G_m^s GSMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	G_m^s Model name
2	As mole-fraction average of solid pure component Gibbs free energy and excess Gibbs free energy $\sum_i x_i^s \mu_i^{*,s} + G_m^{E,s} + RT \sum_i x_i^s \ln x_i^s$	$\mu_i^{*,s}$ Route ID $G_m^{E,s}$ Route ID (Default: $G_m^{E,s} = 0$)
3	From ideal gas Gibbs free energy and solid Gibbs free energy depature $G_m^{ig} + (G_m^s - G_m^{ig})$	
4	From solid pure component Gibbs free energy $\mu_i^{*,s}$ using a mixing rule	$\mu_i^{*,s}$ Route ID G_m^s Model name used to provide mixing rules for the pure component property $\mu_i^{*,s}$

Solid Mixture Molar Gibbs Free Energy Departure

$G_m^s - G_m^{ig}$ DGSMX (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(G_m^s - G_m^{ig})$ Model name
2	From mole-fraction average of pure component Gibbs free energy departure and excess Gibbs free energy $\sum_i x_i^s \left(\mu_i^{*,s} - \mu_i^{*,ig}\right) + G_m^{E,s}$	$(\mu_i^{*,s} - \mu_i^{*,ig})$ Route ID $G_m^{E,s}$ Route ID (Default: $G_m^{E,s} = 0$)

Solid Mixture Molar Excess Gibbs Free Energy

$G_m^{E,s}$ GSXS (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$G_m^{E,s}$ Model name
2	From solid activity coefficient $RT \sum_i x_i^s \ln \gamma_i^s$	γ_i Model name

Vapor Entropy Methods

Vapor Pure Component Molar Entropy

$S_i^{*,v}$ SV (major property)

Method Code	Method	Route Structure Information Required
1	From vapor enthalpy and vapor Gibbs free energy $\frac{1}{T}\left(H_i^{*,v} - \mu_i^{*,v}\right)$	$H_i^{*,v}$ Route ID
2	From ideal gas entropy and vapor entropy departure $S_i^{*,ig} + (S_i^{*,v} - S_i^{*,ig})$	$(S_i^{*,v} - S_i^{*,ig})$ Route ID (Default: $S_i^{*,v} - S_i^{*,ig} = 0$)
3	Directly by a model	$S_i^{*,v}$ Model name

Vapor Pure Component Molar Entropy Departure

$S_i^{*,v} - S_i^{*,ig}$ DSV (subordinate property)

Method Code	Method	Route Structure Information Required
1	From enthalpy departure and Gibbs free energy departure $\left(\frac{H_i^{*,v} - H_i^{*,ig}}{T}\right) - \left(\frac{\mu_i^{*,v} - \mu_i^{*,ig}}{T}\right)$	$(H_i^{*,v} - H_i^{*,ig})$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) $(\mu_i^{*,v} - \mu_i^{*,ig})$ Route ID (Default: $\mu_i^{*,v} - \mu_i^{*,ig} = 0$)
2	From the temperature derivative of Gibbs free energy departure $-\frac{\partial}{\partial T}\left(\mu_i^{*,v} - \mu_i^{*,ig}\right)$	$(\mu_i^{*,v} - \mu_i^{*,ig})$ Model name
3	Directly by a model	$S_i^{*,v} - S_i^{*,ig}$ Model name

Vapor Mixture Molar Entropy

S_m^v SVMX (major property)

Method Code	Method	Route Structure Information Required
1	From vapor enthalpy and vapor Gibbs free energy $\frac{1}{T}(H_m^v - G_m^v)$	H_m^vRoute ID G_m^vRoute ID

Method Code	Method	Route Structure Information Required
2	From ideal gas entropy and vapor entropy departure $S_m^{ig} + (S_m^v - S_m^{ig})$	$(S_m^v - S_m^{ig})$ Route ID (Default: $S_m^v - S_m^{ig} = 0$)
3	Directly by a model	S_m^v Model name

Vapor Mixture Molar Entropy Departure

$S_m^v - S_m^{ig}$ DSVMX (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(S_m^v - S_m^{ig})$ Model name
2	From enthalpy departure and Gibbs free energy departure $\left(\frac{H_m^v - H_m^{ig}}{T}\right) - \left(\frac{G_m^v - G_m^{ig}}{T}\right)$	$(H_m^v - H_m^{ig})$ Route ID (Default: $H_m^v - H_m^{ig} = 0$) $(G_m^v - G_m^{ig})$Route ID (Default $G_m^v - G_m^{ig} = 0$)
3	From the temperature derivative of Gibbs free energy departure $-\frac{\partial}{\partial T}\left(G_m^v - G_m^{ig}\right)$	$(G_m^v - G_m^{ig})$ Model name
4	Directly by an equation-of-state model that uses advanced mixing rules, using a gamma model $S_m^v - S_m^{ig} = f(\gamma_i)$	γ_i Model name Equation of state model name

Liquid Entropy Methods

Liquid Pure Component Molar Entropy

$S_i^{*,l}$ SL (major property)

Method Code	Method	Route Structure Information Required
1	From liquid enthalpy and liquid Gibbs free energy $\frac{1}{T}\left(H_i^{*,l} - \mu_i^{*,l}\right)$	$H_i^{*,l}$ Route ID $\mu_i^{*,l}$ Route ID

Method Code	Method	Route Structure Information Required
2	From ideal gas entropy and liquid entropy departure $S_i^{*,ig} + (S_i^{*,l} - S_i^{*,ig})$	$(S_i^{*,l} - S_i^{*,ig})$ Route ID
3	Directly from a model	$S_i^{*,l}$ Model name

Liquid Pure Component Molar Entropy Departure

$S_i^{*,l} - S_i^{*,ig}$ DSL (subordinate property)

Method Code	Method	Route Structure Information Required
1	From enthalpy departure and Gibbs free energy departure $\left(\frac{H_i^{*,l} - H_i^{*,ig}}{T}\right) - \left(\frac{\mu_i^{*,l} - \mu_i^{*,ig}}{T}\right)$	$(H_i^{*,l} - H_i^{*,ig})$ Route ID
2	From the temperature derivative of Gibbs free energy departure $-\frac{\partial}{\partial T}\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$	$(\mu_i^{*,l} - \mu_i^{*,ig})$ Route ID $(\mu_i^{*,l} - \mu_i^{*,ig})$ Model name
3	Directly by a model	$(S_i^{*,l} - S_i^{*,ig})$ Model name

Liquid Mixture Molar Entropy

S_m^l SLMX (major property)

Method Code	Method	Route Structure Information Required
1	From liquid enthalpy and liquid Gibbs free energy $\frac{1}{T}\left(H_m^l - G_m^l\right)$	H_m^l Route ID G_m^l Route ID
2	From ideal gas entropy and liquid entropy departure $S_m^{ig} + (S_m^l - S_m^{ig})$	$(S_m^l - S_m^{ig})$ Route ID
3	Directly by a model	S_m^l Model name
4	By an electrolyte model $S_m^l = f(H_m^l, G_m^l, x^t)$	H_m^l model G_m^l model x^t Route ID
5	From liquid enthalpy and liquid Gibbs free energy $\frac{1}{T}\left(H_m^l - G_m^l\right)$ for electrolyte system	H_m^l Route ID G_m^l Route ID

Liquid Mixture Molar Entropy Departure

$S_m^l - S_m^{ig}$ DSLMX (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	($S_m^l - S_m^{ig}$) Model name
2	From enthalpy departure and Gibbs free energy departure $\left(\frac{H_m^l - H_m^{ig}}{T}\right) - \left(\frac{G_m^l - G_m^{ig}}{T}\right)$	($H_m^l - H_m^{ig}$) Route ID ($G_m^l - G_m^{ig}$) Route ID
3	From the temperature derivative of Gibbs free energy departure $-\frac{\partial}{\partial T}\left(G_m^l - G_m^{ig}\right)$	($G_m^l - G_m^{ig}$) Model name
4	Directly by an equation-of-state model using advanced mixing rules using a gamma model $S_m^l - S_m^{ig} = f(\gamma_i)$	γ_i Model name Equation of state model name

Solid Entropy Methods

Solid Pure Component Molar Entropy

$S_i^{*,s}$ SS (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$S_i^{*,s}$ Model name
2	From solid enthalpy and solid Gibbs free energy $\frac{1}{T}\left(H_i^{*,s} - \mu_i^{*,s}\right)$	$H_i^{*,s}$ Route ID $\mu_i^{*,s}$ Route ID

Solid Pure Component Molar Entropy Departure

$S_i^{*,s} - S_i^{*,ig}$ DSS (subordinate property)

Method Code	Method	Route Structure Information Required
1	From pure component enthalpy departure and pure component Gibbs free energy departure $\left(\frac{H_i^{*,s}-H_i^{*,ig}}{T}\right)-\left(\frac{\mu_i^{*,s}-\mu_i^{*,ig}}{T}\right)$	$(H_i^{*,s} - H_i^{*,ig})$ Route ID $(\mu_i^{*,s} - \mu_i^{*,ig})$ Route ID
2	Directly by a model	$(S_i^{*,s} - S_i^{*,ig})$ Model name

Solid Mixture Molar Entropy

S_m^s SSMX (major property)

Method Code	Method	Route Structure Information Required
1	From solid enthalpy and solid Gibbs free energy $\frac{1}{T}(H_m^s - G_m^s)$	H_m^s Route ID G_m^s Route ID
2	From ideal gas entropy and solid entropy departure $S_m^{ig} + (S_m^s - S_m^{ig})$	$(S_m^s - S_m^{ig})$ Route ID

Solid Mixture Molar Entropy Departure

$S_m^s - S_m^{ig}$ DSSMX (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(S_m^s - S_m^{ig})$ Model name
2	From enthalpy departure and Gibbs free energy depature $\left(\frac{H_m^s-H_m^{ig}}{T}\right)-\left(\frac{G_m^s-G_m^{ig}}{T}\right)$	$(H_m^s - H_m^{ig})$ Route ID $(G_m^s - G_m^{ig})$ Route ID
3	From temperature derivative of Gibbs free energy departure $-\frac{\partial}{\partial T}\left(G_m^s - G_m^{ig}\right)$	$(G_m^s - G_m^{ig})$ Model name

Molar Volume Methods

Vapor Pure Component Molar Volume

$V_i^{*,v}$ VV (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$V_i^{*,v}$ Model name

Vapor Mixture Molar Volume

V_m^v VVMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	V_m^v Model name
2	From vapor pure component molar volume using mixing rules $V_m^v = f(y_i, V_i^{*,v})$	$V_i^{*,v}$ Route ID V_m^v Model name
3	Directly by an equation-of-state model using advanced mixing rules using a gamma model $V_m^v = f(\gamma_i)$	γ_i Model name γ_i Model name (eos only)

Liquid Pure Component Molar Volume

$V_i^{*,l}$ VL (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$V_i^{*,l}$ Model name

Liquid Mixture Molar Volume

V_m^l VLMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	V_m^l Model name
2	From liquid pure component molar volume using mixing rules $V_m^l = f(x_i, V_i^{*,l})$	$V_i^{*,l}$ Route ID V_m^l Model name
3	By an electrolyte model which uses true compositions (x^t)	$V_i^{*,l}$ Model name x^t Route ID
4	Directly by an equation-of-state model using advanced mixing rules using a gamma model $V_m^l = f(\gamma_i)$	γ_i Model name V_m^l Model name (eos only)

Solid Pure Component Molar Volume

$V_i^{*,s}$ VS (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$V_i^{*,s}$ Model name

Solid Mixture Molar Volume

V_m^s VSMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	V_m^s Model name
2	From solid pure component molar volume using mixing rules $V_m^s = f(x_i^s, V_i^{*,s})$	$V_i^{*,s}$ Route ID V_m^s Model name

Viscosity Methods

Vapor Pure Component Viscosity

$\eta_i^{*,v}$ MUV (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$\eta_i^{*,v}$ Model name
2	From low pressure vapor viscosity $\eta_i^{*,v} = \eta_i^{*,v}(p=0)$	$(\eta_i^{*,v}(p=0))$ Route ID
3	From vapor volume $\eta_i^{*,v} = f(V_i^{*,v})$	$V_i^{*,v}$ Route ID $\eta_i^{*,v}$ Model name
4	From low pressure vapor viscosity and pressure correction $\eta_i^{*,v} = \eta_i^{*,v}(p=0) + (\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0))$	$(\eta_i^{*,v}(p=0))$ Route ID $(\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0))$ Route ID

Low Pressure Vapor Pure Component Viscosity

$\eta_i^{*,v}(p=0)$ MUVLP (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\eta_i^{*,v}(p=0))$ Model name

Vapor Pure Component Viscosity Pressure Correction

$\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0)$ MUVPC (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0))$ Model name
2	From vapor volume $(\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0)) = f(V_i^{*,v})$	$V_i^{*,v}$ Route ID Model name

Vapor Mixture Viscosity

η^v MUVMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	η^v Model name
2	From vapor pure component viscosity using mixing rules $\eta^v = f(y_i,\eta_i^{*,v})$	$\eta_i^{*,v}$ Route ID η^v Model name
3	From low pressure vapor mixture viscosity $\eta^v = \eta^v(p=0)$	$(\eta^v\ (p=0))$ Route ID
4	From vapor mixture volume $\eta^v = f(V_m^v)$	V_m^v Route ID
5	From low pressure vapor mixture viscosity and pressure correction $\eta_i^v = \eta_i^v(p=0)$ $+ (\eta_i^v(p) - \eta_i^v(p=0))$	η^v Model name $(\eta^v\ (p=0))$ Route ID $(\eta_i^v(p) - \eta_i^v(p=0))$ Route ID

Low Pressure Vapor Mixture Viscosity

$\eta^v\ (p=0)$ MUVMXLP (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\eta^v\ (p=0))$ Model name
2	From low pressure vapor pure component viscosity $(\eta^v\ (p=0)) = f(y_i,\eta_i^{*,v}(p=0))$	$(\eta_i^{*,v}\ (p=0))$ Route ID $(\eta^v\ (p=0))$ Model name

Vapor Mixture Viscosity Pressure Correction

$\eta^v(p) - \eta^v(p=0)$ MUVMXPC (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\eta^v(p) - \eta^v(p=0))$ Model name
2	From vapor mixture volume $(\eta^v(p) - \eta^v(p=0)) = f(V_m{}^v)$	$V_m{}^v$ Route ID $(\eta^v(p) - \eta^v(p=0))$ Model name

Liquid Pure Component Viscosity

$\eta_i{}^{*,l}$ MUL (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$\eta_i{}^{*,l}$ Model name
2	From liquid volume $\eta_i{}^{*,l} = f(V_i{}^{*,l})$	$V_i{}^{*,l}$ Route ID $\eta_i{}^{*,l}$ Model Name

Liquid Mixture Viscosity

η^l MULMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	η^l Model name
2	From liquid pure component viscosity using mixing rules $\eta^l = f(x_i, \eta_i{}^{*,l})$	$\eta_i{}^{*,l}$ Route ID η^l Model name
3	From liquid mixture volume $\eta^l = f(V_m{}^l)$	$V_m{}^l$ Route ID η^l Model name
4	Directly by an electrolyte model (x^t)	η^l Model name x^t Route ID

Thermal Conductivity Methods

Vapor Pure Component Thermal Conductivity

$\lambda_i{}^{*,v}$ KV (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$\lambda_i{}^{*,v}$ Model name

Method Code	Method	Route Structure Information Required
2	From low pressure vapor thermal conductivity $\lambda_i^{*,v} = (\lambda_i^{*,v}(p{=}0))$	$(\lambda_i^{*,v}(p{=}0))$ Route ID
3	From low pressure vapor thermal conductivity and pressure correction $\lambda_i^{*,v} = (\lambda_i^{*,v}(p{=}0))$ $+ (\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p{=}0))$	$(\lambda_i^{*,v}(p{=}0))$ Route ID $(\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p{=}0))$ Route ID
4	From vapor volume and low pressure vapor viscosity $\lambda_i^{*,v} = f(V_i^{*,v}, \eta_i^{*,v}(p{=}0))$	$V_i^{*,v}$ Route ID $(\eta_i^{*,v}(p{=}0))$ Model name $\lambda_i^{*,v}$ Model Name

Low Pressure Vapor Pure Component Thermal Conductivity

$\lambda_i^{*,v}(p{=}0)$ KVLP (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\lambda_i^{*,v}(p{=}0))$ Model name
2	From low pressure vapor viscosity $\lambda_i^{*,v}(p{=}0) = f(\eta_i^{*,v}(p{=}0))$	$(\eta_i^{*,v}(p{=}0))$ Route ID $\lambda_i^{*,v}$ Model name

Vapor Pure Component Thermal Conductivity Pressure Correction

$\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p{=}0)$ KVPC (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p{=}0))$ Model name
2	From vapor volume $(\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p{=}0)) = f(V_i^{*,v})$	$V_i^{*,v}$ Route ID $(\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p{=}0))$ Model name

Vapor Mixture Thermal Conductivity

λ^v KVMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	λ^v Model name

Method Code	Method	Route Structure Information Required
2	From vapor pure component thermal conductivity using mixing rules $\lambda^v = f(y_i, \lambda_i^{*,v})$	$\lambda_i^{*,v}$ Route ID λ^v Model name
3	From low pressure vapor mixture thermal conductivity $\lambda^v = (\lambda^v(p=0))$	$(\lambda^v(p=0))$ Route ID
4	From low pressure vapor mixture thermal conductivity and pressure correction $\lambda^v = (\lambda^v(p=0))$ $+ (\lambda^v(p) - \lambda^v(p=0))$	$(\lambda^v(p=0))$ Route ID $(\lambda^v(p) - \lambda^v(p=0))$ Route ID
5	From vapor mixture volume and low pressure vapor mixture viscosity $\lambda^v = f(V_m^v, \eta^v(p=0))$	V_m^v Route ID $(\eta^v(p=0))$ Route ID λ^v Model name

Low Pressure Vapor Mixture Thermal Conductivity

$\lambda^v(p=0)$ KVMXLP (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\lambda^v(p=0))$ Model name
2	From low pressure pure component vapor thermal conductivity and viscosity $\lambda^v(p=0) =$ $f(y_i, \lambda_i^{*,v}(p=0), \eta_i^{*,v}(p=0))$	$\lambda_i^{*,v}$ Route ID $(\eta_i^{*,v}(p=0))$ Route ID $(\lambda^v(p=0))$ Model name

Vapor Mixture Thermal Conductivity Pressure Correction

$\lambda^v(p) - \lambda^v(p=0)$ KVMXPC (subordinate property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$(\lambda^v(p) - \lambda^v(p=0))$ Model name
2	From vapor mixture volume $(\lambda^v(p) - \lambda^v(p=0)) = f(V_m^v)$	V_m^v Route ID $(\lambda^v(p) - \lambda^v(p=0))$ Model name

Liquid Pure Component Thermal Conductivity

$\lambda_i^{*,l}$ KL (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$\lambda_i^{*,l}$ Model name
2	From liquid volume and low pressure vapor viscosity $\lambda_i^{*,l} = f(V_i^{*,l}, \eta_i^{*,v}(p=0))$	$V_i^{*,l}$ Route ID $(\eta_i^{*,v}(p=0))$ Route ID $\lambda_i^{*,l}$ Model name

Liquid Mixture Thermal Conductivity

λ^l KLMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	λ^l Model name
2	From liquid pure component thermal conductivity using mixing rules $\lambda^l = f(x_i, \lambda_i^{*,l})$	$\lambda_i^{*,l}$ Route ID λ^l Model name
3	From liquid mixture volume and low pressure vapor mixture viscosity $\lambda^l = f(V_m^l, \eta^v(p=0))$	V_m^l Route ID $(\eta^v(p=0))$ Route ID λ^l Model name
4	Directly by an electrolyte model (x^t)	λ^l Model name x^t Route ID

Solid Pure Component Thermal Conductivity

$\lambda_i^{*,s}$ KS (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	$\lambda_i^{*,s}$ Model name

Solid Mixture Thermal Conductivity

λ^s KSMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	λ^s Model name
2	From solid pure component thermal conductivity using mixing rules $\lambda^s = f(x_i^s, \lambda_i^{*,s})$	$\lambda_i^{*,s}$ Route ID λ^s Model name

Diffusion Coefficient Methods

Vapor Binary Diffusion Coefficient

D_{ij}^{v} DV (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	D_{ij}^{v} Model name

Vapor Diffusion Coefficient for a Component in a Mixture

D_i^{v} DVMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	D_i^{v} Model name
2	From vapor binary diffusion coefficients $D_i^{v} = f(y_i, D_{ij}^{v})$	D_{ij}^{v} Route ID y_i Model name

Liquid Binary Diffusion Coefficient

D_{ij}^{l} DL (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	Model name
2	From liquid mixture viscosity η^{l}	η^{l} Route ID D_{ij}^{l} Model name

Liquid Diffusion Coefficient for a Component in a Mixture

D_i^{l} DLMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	Model name
2	From liquid binary diffusion coefficients $D_i^{l} = f(x_i, D_{ij}^{l})$	D_{ij}^{l} Route ID D_i^{l} Model name
3	From liquid mixture viscosity $D_i^{l} = f(x_i, \eta^{l})$	η^{l} Route ID D_i^{l} Model name
4	Directly by an electrolyte model (x^{t})	D_i^{l} Model name x^{t} Route ID

Surface Tension Methods

Liquid Pure Component Surface Tension

$\sigma_i^{*,l}$ SIGL (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	Model name

Liquid Mixture Surface Tension

σ^l SIGLMX (major property)

Method Code	Method	Route Structure Information Required
1	Directly by a model	Model name
2	From pure component surface tension using mixing rules $\sigma^l = f(x_i, \sigma_i^{*,l})$	$\sigma_i^{*,l}$ Route ID σ^l Model name
3	Directly by an electrolyte model (x^t)	σ^l Model name x^t Route ID

Routes And Models

This section explains the structure of physical property calculations by showing the relationship between models and routes, and between routes on different levels. It also explains how to trace a calculation route.

Concept of Routes

A route is a technique for calculating a particular property. It consists of one of the methods described in the tables in the Methods section along with the information needed to perform that calculation.

The technique contained in a route may depend on other properties. If a route requires a major or subordinate property, then an additional, sub-level route is specified within the route for calculating that other property. If a route requires an intermediate property, then the model required for calculating that property is specified within the route. A route may also simply consist of a model that directly calculates the property. If a model used in a route has model option codes, these are specified in the route as well.

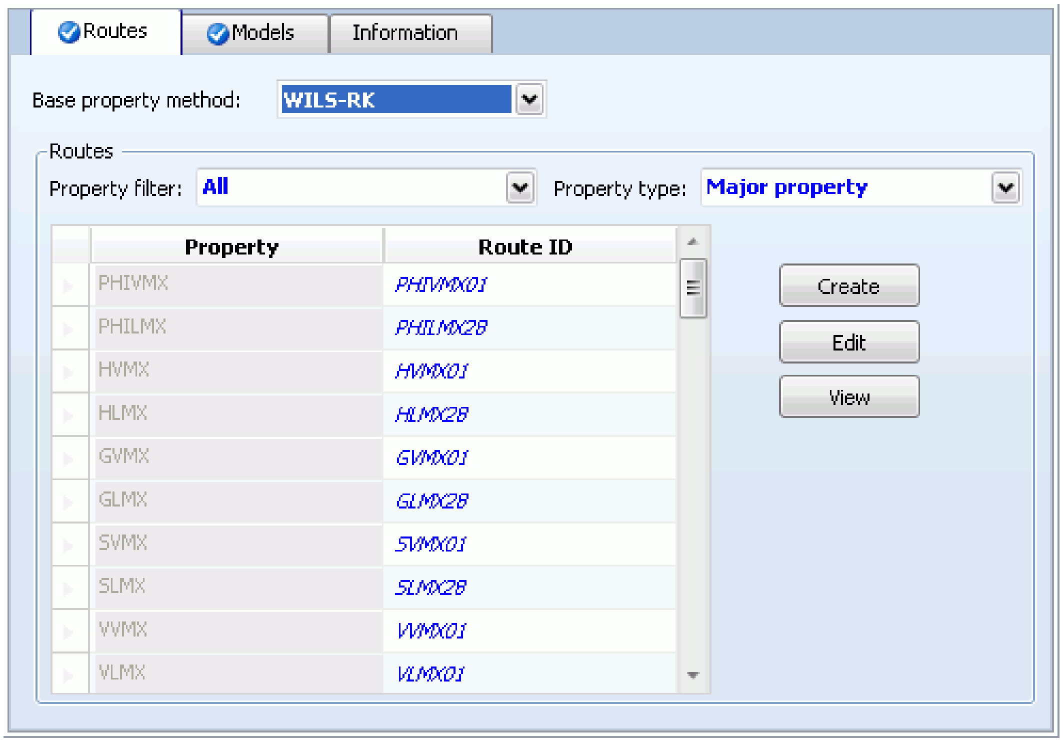
The collection of all this information is called a route. Since routes can depend on other routes, and those routes may in turn depend on yet other routes, a multi-level tree of routes may exist under a single route. Example 1 discusses a route that does *not* depend on other routes. See Example 2 for a route which depends on a secondary route.

Models consist of the equations needed to calculate a property from state variables and parameters. They do not depend on other routes, and make up the end branches of the tree of routes.

Each built in route in the Aspen Physical Property System has a unique route ID, which is composed of the property name (as described in the tables of Major Properties, Subordinate Properties, and Intermediate Properties) and a number, for example HLMX10.

Route IDs associated with the route information represent a unique combination of sub-level routes and models. Therefore, a top-level route ID specifies the full calculation tree. Because of the uniqueness of route IDs, you can use them for documenting your calculation. See Tracing a Route to learn how to follow the tree of routes, and see an example of such a tree.

A property method can calculate a fixed list of properties (see Physical Properties in the Aspen Physical Property System). The calculation procedure of *each* property constitutes a route and has a route ID. Therefore, a property method consists of a collection of the route IDs of the properties it can calculate. The **Methods | Selected Methods | Routes** sheet shows the routes used in a property method. If you want to see all of the built-in routes available for calculating a property listed in the **Property** column, open the list in the corresponding **Route ID** field. Select any route on this sheet and click **View** to see the tree of routes and models under this route.



Base property method: WILS-RK

Property filter: All

Property type: Major property

Property	Route ID
PHIVMX	PHIVMX01
PHILMX	PHILMX28
HVMX	HVMX01
HLMX	HLMX28
GVMX	GVMX01
GLMX	GLMX28
SVMX	SVMX01
SLMX	SLMX28
VVMX	VVMX01
VLMX	VLMX01

Properties Property Methods Routes Sheet

Example 1 shows route information for PHILMX, method 1. Example 2 shows Route information for HLMX, method 3.

If necessary, you can define your own routes. See Modifying and Creating Routes.

Example 1: Route information for PHILMX, method 1

The first method from the table labeled Liquid Fugacity Coefficient Methods for the calculation of the fugacity coefficient of component in a liquid mixture is *specified model*. This model can be an equation of state model that calculates the fugacity coefficient as a function of state variables and correlation parameters:

$\varphi_i^l = f(p, T, x_i, \text{correlation parameters})$

There are many models that can be used to calculate φ_i^l, such as the Redlich-Kwong-Soave model, the Peng-Robinson model, and the Hayden O'Connell model. It is sufficient to select a model name in order to completely specify a route according to this method.

Example 2: Route information for HLMX, method 3

The third method for calculating the liquid mixture enthalpy H_m^l (see the table labeled Liquid Enthalpy Methods) is:

$H_m^l = H_m^{ig} + (H_m^l - H_m^{ig})$

In this method, H_m^l depends on the ideal gas enthalpy and the enthalpy departure $H_m^l - H_m^{ig}$, a subordinate property. The table labeled Liquid Enthalpy Methods indicates in the rightmost column that the required information is the route ID for the subordinate property. Specifying this route means that the top-level route now refers to a sub-level route ID.

For all methods that use both an ideal gas contribution and a departure function, the Aspen Physical Property System automatically fills in the ideal gas calculation. You need to specify only the departure function.

To specify the sub-level route for the enthalpy departure, you must choose a method. For example, you might choose method 1: specified model (see the table labeled Liquid Enthalpy Methods). For this method, the required information is the model name, such as the Redlich-Kwong-Soave equation-of-state model.

Models

A model consists of one or more equations to evaluate a property, and has state variables, universal parameters, and correlation parameters as input variables. In contrast to methods (as described in Concept of Routes, above) which are based only on universal scientific principles, models are much more arbitrary in nature, and often have constants which need to be determined by data fitting. An example of a model is the Extended Antoine vapor pressure equation (see *Physical Property Models*). Equations of state have built in correlation parameters and are also models.

Models are sometimes used in multiple routes of a property method. For example, an equation-of-state model can be used to calculate all vapor and liquid departure functions of an equation-of-state based property method. The Rackett model can be used to calculate the pure component and mixture liquid molar volumes, ($V_i^{*,l}$ and V_m^l), and it can also be used in the calculation of the Poynting correction factor, as part of the calculation of the pure component liquid fugacity coefficient.

The **Methods | Selected Methods | Models** sheet (shown below) displays the models that are globally used in the routes of the selected property method. Changing routes on the **Methods | Selected Methods | Routes** sheet causes the **Models** sheet to be rewritten based on the new set of routes, so you should specify all routes before specifying any models on the **Models** sheet.

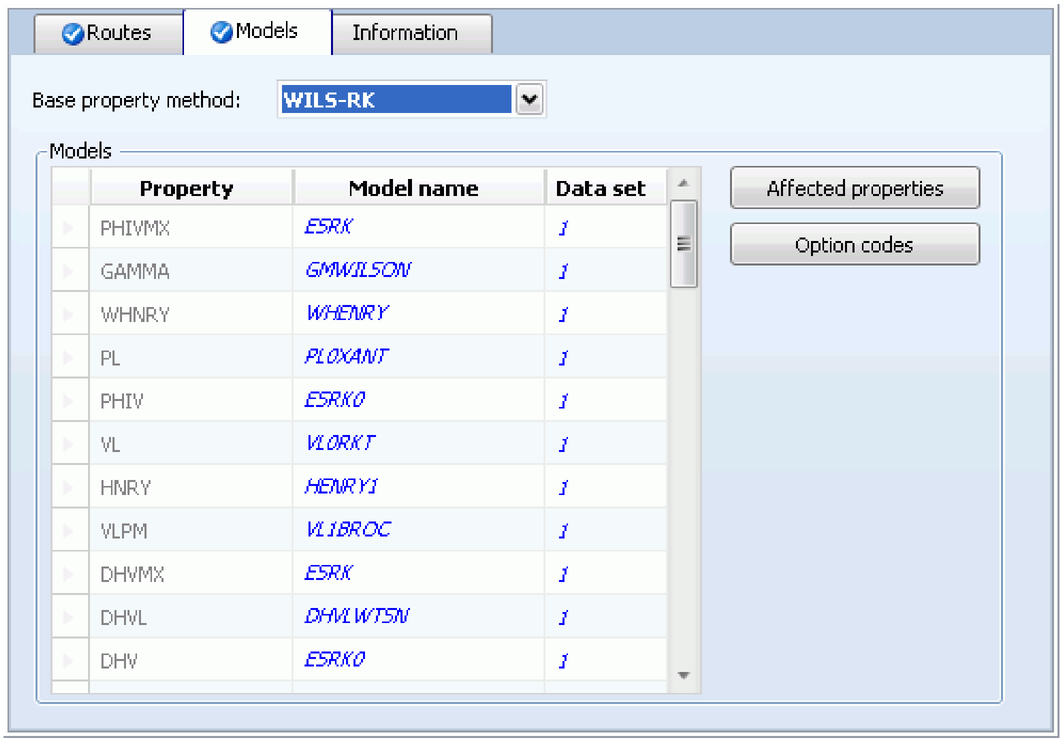
Note: Some advanced equation-of-state models depend on an activity coefficient (GAMMA) model to calculate activity coefficients. These models cannot be used on their own, and should only be included in a method by selecting an appropriate route on the **Routes** sheet. The models in question are ones related to the Wong-Sandler, MHV2, PSRK, and VTPR models: ESPRWS, ESPRV1, ESPRV2, ESPRWS0, ESPRV10, ESPRV20, ESRKSWS, ESRKSV1, ESRKSV2, ESRKSWS0, ESRKSV10, ESRKSV20, ESVTPR, ESVTPR0.

Sometimes, different routes in a method which calculate the same property (one or both as intermediate steps in calculating some other property) may use different models to calculate the property. In that case, the property will be listed more than once on the **Models** sheet, with each applicable model listed.

For a given model, click the **Affected properties** button to display a list of properties which are affected by the model calculations. Open the list in a **Model Name** field to display a list of all available models for a specific property.

Note: Changing a model on this sheet causes it to be used for all properties which it can calculate, overriding the methods specified by routes. If a property appears more than once, changing the model here affects calculation for all instances of the property. To specify models only for specific properties, use routes instead. If necessary, you can create your own routes; see Modifying and Creating Routes for details.

You can also use the tables labeled Thermodynamic Property Models, Transport Property Models, and Nonconventional Solid Property Models in *Physical Property Models*. If you need to use a proprietary model or a new model from the literature, you can interface these to the Aspen Physical Property System (see *Aspen Plus User Models*.)



Base property method: WILS-RK

Property	Model name	Data set
PHIVMX	ESRK	1
GAMMA	GMWILSON	1
WHNRY	WHENRY	1
PL	PL0XANT	1
PHIV	ESRK0	1
VL	VL0RKT	1
HNRY	HENRY1	1
VLPM	VL1BROC	1
DHVMX	ESRK	1
DHVL	DHVLWTSN	1
DHV	ESRK0	1

Methods | Selected Methods | Models Sheet

Some models have model option codes to specify different possible calculation options. For example, the model WHNRY has three options to calculate the weighting factor from the critical molar volume. The calculation option is identified by the model option code. On the **Selected Methods | Models** sheet, first select the model, then click the **Option codes** button to display a list of option code values for the model. See Property Model Option Codes in *Physical Property Models* for descriptions of the option codes.

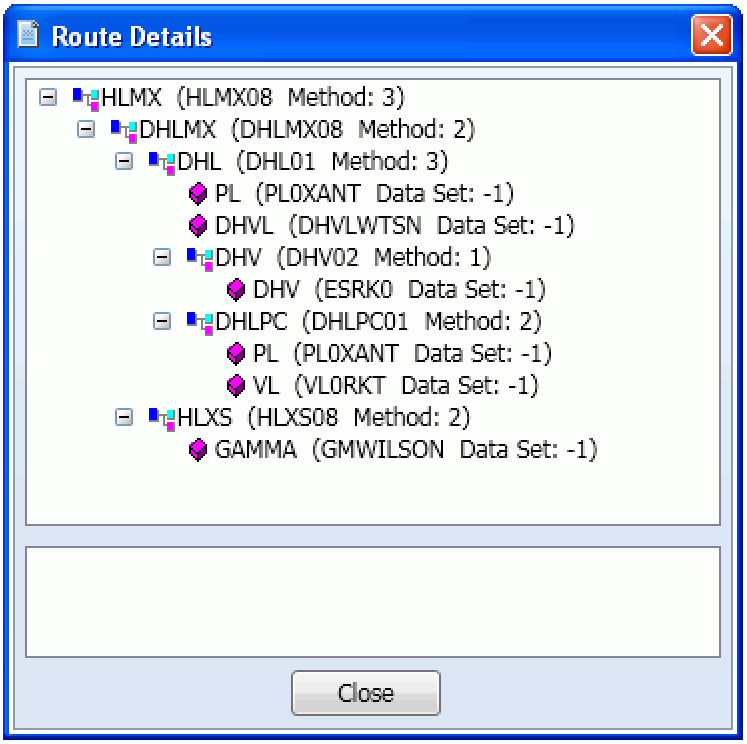
Tracing a Route

The structure of a full calculation route is generally shaped as a tree control. Each point in the tree where a branch splits off (a node) represents a method. The branches themselves are the routes. The ends of the branches are models. The starting point for tracing a route is usually finding a route ID on the Property Methods Routes sheet, for which you want to know the calculation procedure. Example 1 describes how you can trace a known route ID.

Example 1: Tracing the route HLMX08

The route ID is on the **Methods | Selected Methods | Routes** sheet for the Wilson property method. It appears in the second column, next to the property HLMX: HLMX08 (a similar sheet is shown in the figure labeled Properties Property Methods Routes Sheet).

Click on the property HLMX or the route ID HLMX08, then click **View**. The **Route Details** dialog box appears.



- HLMX (HLMX08 Method: 3)
  - DHLMX (DHLMX08 Method: 2)
    - DHL (DHL01 Method: 3)
      - PL (PL0XANT Data Set: -1)
      - DHVL (DHVLWTSN Data Set: -1)
      - DHV (DHV02 Method: 1)
        - DHV (ESRK0 Data Set: -1)
      - DHLPC (DHLPC01 Method: 2)
        - PL (PL0XANT Data Set: -1)
        - VL (VL0RKT Data Set: -1)
    - HLXS (HLXS08 Method: 2)
      - GAMMA (GMWILSON Data Set: -1)

If you click on a route or model on the tree, a short description of the route or model appears at the bottom of the dialog box. At the first node, the route HLMX08 appears, which uses method 3. In this method, the liquid mixture enthalpy is calculated from the ideal gas enthalpy and the enthalpy departure. The Aspen Physical Property System automatically fills in the ideal gas calculations. Only the departure function route ID must be specified. Therefore, there is only one branch attached to the node for route HLMX08.

The next step in the route HLMX08 is the calculation of the liquid mixture enthalpy departure with route ID: DHLMX08. This calculation is based on method 2, which calculates DHLMX as the mole fraction average of pure component enthalpy departure (DHL) and the excess enthalpy (HLXS). Therefore, two branches split from this route. The complete route can be traced this way.

These two steps in tracing the route HLMX08 show that a route ID is characteristic for the methods, routes and models specified on its own level. However, by specifying DHLMX08 on the top level, the top level route is also characteristic for the level below because DHLMX08 stands for a full specification on its secondary level. If we continue this reasoning down the tree to the models, then it becomes clear that HLMX08 represents the full specification of the full tree. And DHLMX08 represents the full specification of the full tree, minus the top level. Therefore every built in route has a unique ID. This feature will be used in Modifying and Creating Routes.

Method Numbers

To look up the equation corresponding to the method number of a route, look up the method in the table Methods tables. For instance, find HLMX in the table labeled Vapor Fugacity Coefficient Methods. The formula is listed next to the method number.

Modifying and Creating Property Methods

The built in property methods in the Aspen Physical Property System contain choices of major property routes that fit most engineering needs. The combinations of the routes for different properties are chosen in a logical way, as explained in Classifications of Property methods and Recommended Use in Property Method Descriptions. You may sometimes need to customize property methods. For example, to change models or routes on a main or a sub level. This section explains how to do this and gives examples of how to implement the most frequently used modifications.

Modifying Existing Property Methods

The following subsections explain the different types of modifications that can be made to property methods.

- Replacing Routes
- Replacing Models and Using Multiple Data Sets
- Conflicting Route and Model Specifications

Replacing Routes

The **Selected Methods | Routes** sheet allows you to see which routes are used in a certain property method and to trace a route (see Routes and Models). This form also allows you to replace routes. A route replacement influences the calculations of one property at a time.

To replace routes:

1. In the navigation pane, open **Methods**, then click **Selected Methods**.
   The Selected Methods Object Manager appears.
2. Select the property method and click **Edit**.
   The **Selected Methods** form appears.
3. Go to the **Routes** sheet.
4. In the **Route ID** field of the property of interest, click to list all available routes for this property.

As you scroll through the list, the prompt displays a short description of the route. When you gain experience, the description from the prompt should be sufficient. If you require more information,

   - Select the route, then click the **View** button to get the tree diagram for this route (see Routes and Models). You can now trace the route in detail.
   - Close the **View Route** dialog box to return to the **Routes** sheet.

5. Select a route that fits your needs.

   The newly selected route changes color, so that you are able to locate your property method modifications immediately on this sheet.

The technique is identical for subordinate properties.

Example 1: Using COSTALD liquid molar volume in PENG-ROB

In the PENG ROB property method, the Rackett equation is used for the liquid molar volume (route VLMX01, property VLMX). For high pressure calculations, use the COSTALD model which is suited for compressed liquids. The route selected is VLMX22. For consistency with pure component results, replace the VL calculation with VL06.

Example 2: Using Lee-Kesler liquid volume in RK-Soave

For a high pressure hydrocarbon application, use the Lee Kesler liquid molar volume calculation rather than the atmospheric API density calculation. Select VLMX13 for VLMX. No corresponding pure component routes are available, since these calculations are for complex petroleum mixtures, of which the pure components are only partially known.

Example 3: Using ideal mixing for the liquid molar volume in WILSON

You want to compare the Rackett mixture equation with ideal mixing. The pure component liquid molar volume should remain as it is (Model: VL0RKT, Route ID: VL01). Select the route VLMX23 to use the ideal mixing rule (mole fraction average of pure component liquid molar volumes).

Example 4: Removing Poynting correction of an activity coefficient

The Poynting correction is the pressure correction to the pure component liquid fugacity coefficient. For validation purposes, you need to compare your calculation with previous results that have been obtained without the Poynting correction.

In all activity coefficient based property methods with the Redlich Kwong equation of state as the vapor phase model, the route PHIL04 is used for the pure component liquid fugacity coefficient. Tracing **PHIL04** (using the **View** button) shows that the pressure correction is calculated by the subordinate property **PHILPC** with route ID **PHILPC01**.

On the **Selected Methods | Routes** sheet, select **Subordinate property** in the **Property route** field. Locate the property **PHILPC** in the **Property** field, then replace **PHILPC01** with **PHILPC00** (no correction) in the **Route ID** field. If you trace **PHIL04** again (using the **View** button), you will notice that the tree is dynamic; it reflects the changes you made in a sub level route, in this case for PHILPC.

In the activity coefficient based property methods with the ideal gas law as the vapor phase model, the route PHIL00 is used. Tracing **PHIL00** shows that **PHILPC00** is used by default. No changes are needed.

Replacing Models and Using Multiple Data Sets

The **Selected Methods | Models** sheet allows you to see which models are used in a certain property method (see Routes and Models). This sheet also allows you to replace models. Route replacements influence only one property at a time. In contrast, a model replacement influences all the properties that use the same model. You can trace the routes of these properties to determine where exactly the model is used in the calculation. If you want to limit the effect of a model replacement to a single route, you can modify an existing route or create a new route (see Modifying and Creating Routes). Click the **Affected properties** button to see a list of properties affected by the model.

If you need to change both routes and models, you must change the routes first using the **Routes** sheet, then change the models. If you use the **Models** sheet before using the **Routes** sheet, the changes you made on the **Models** sheet will be lost.

To replace models:

1. In the navigation pane, open **Methods**, then click **Selected Methods**.

   The Selected Methods Object Manager appears.
2. Select the property method and click **Edit**.

   The **Selected Methods** form appears.
3. Go to the **Models** sheet.
4. On the **Model name** field of the property of interest, click to see all available models for this property. (You can also use the table labeled Liquid Fugacity Coefficient Methods.)

   As you scroll through the list, the prompt displays a short description of the model.

5. Select a model.

   The newly selected model changes color, so that you are able to locate your property method modifications immediately on this form. All properties using the same model will also be changed.

If you draw a tree diagram of a property in which the new model is used, the modification is also shown (see Tracing a Route).

Conflicting Route and Model Specifications

If you specify a route for a certain property and you also specify a model that calculates a property that is part of the route you specified, the information can be conflicting. In the Aspen Physical Property System both replacements will be executed. The result, in most cases, is that the model takes precedence, but you can always predict the result by analyzing the route and checking if there is an occurrence of this type of model in the tree.

Example 1 describes how to use COSTALD liquid molar volume in PENG-ROB. Example 2 describes how to use Peng Robinson for vapor phase properties in NRTL RK.

Example 1: Using COSTALD liquid molar volume in PENG-ROB: Replacing Models

The reasoning is the same as in Example 1, Replacing Routes. The approach here is to replace the Rackett models (VL0RKT, VL2RKT) by the COSTALD models (VL0CTD, VL2CTD). The result is exactly the same as for the route replacement.

Example 2: Using Peng-Robinson for vapor phase properties in NRTL-RK

You want to use the Peng Robinson equation of state as the vapor phase model of an activity coefficient based property method. Instead of replacing every vapor phase property route, it is more efficient to replace the equation of state model used for all vapor phase properties. In the model field, if you select ESPR for a single vapor phase property, the Aspen Physical Property System replaces all other vapor phase properties by the ESPR model as well. For consistency, use ESPR0 for pure component vapor phase properties.

Creating New Property Methods

The purpose of creating new property methods is not so much to build the collection of routes from scratch, although this is possible. It is more a matter of methodology and documentation of your work. Suppose you make changes to existing property methods, and you have successfully completed your calculations. One year later you may have a similar project where you begin with your old calculation models. You may not remember that the WILSON property method you used is not the standard version. Therefore, it is recommended that you:

1. Create a new property method with an ID similar to the property method on which it is based.
2. Copy the base property method to the new property method
3. Make your changes.

There are two ways to begin the creation of a property method.

The first way to begin is:

1. On the **Methods | Specifications | Global** sheet, select the base property method on the Base method field.
2. Check the **Modify property models** checkbox. The **Modify Property Method** dialog box appears.
3. Enter the new property method name, then click **OK**.
4. Go to the **Methods | Selected Methods** Object Manager.
5. Select the new property method, then click **Edit**.

The second way to begin is:

1. Go to the **Methods | Selected Methods** Object Manager.
2. Click **New** and enter the new property method name.

   The **Selected Methods** form for the new method appears.

Then for both methods do the following steps:

1. Select the **Routes** sheet or **the Models** sheet.
2. On the **Base property method** field, select an existing property method name.

   The Aspen Physical Property System fills in all the routes and models in both sheets.
3. Make your changes.
4. Use the newly created property method in a flowsheet, a block, a property analysis, or a column section.

Using Multiple Data Sets in Multiple Property Methods

For most models, it is possible to specify multiple data sets (multiple sets of values for a parameter for the same component). In the tables of parameters in Physical Property Models, the MDS column indicates with an X the parameters which support a second data set.

To use a second data set with a model:

1. From the navigation pane, open **Methods**, then click **Selected Methods**.

   The Selected Methods Object Manager appears.
2. Select the property method and click **Edit**.

   The **Selected Methods** form appears.
3. Go to the **Models** sheet.

   The **Data Set** column is to the right of the **Model** name column. The default for a data set number is 1.
4. Change the data set number to 2 to introduce a second set of parameters for a model.

A second data set is frequently used for activity coefficient models. For example, the VLE are calculated with one set of parameters, the LLE with another set. If you introduce a second data set for an activity coefficient model, it is effective throughout the property method. To use two data sets in different parts of the flowsheet or a distillation column, you must use two property methods: one property method that uses the default data set 1, and another property method that uses the data set 2. If you create a second data set for a model, the Aspen Physical Property System automatically defines the second set of parameters on the **Methods | Parameters** forms. So you must enter the parameters values for the second data set after creating the property method in which they are to be used.

Note: Data set *n*+1 defaults to data set *n*. This means that if you do not enter all parameters in the second data set, parameters from the first data set may be used where they are missing in the second data set. The reverse is not true. In general, if parameters in a data set are missing, the Aspen Physical Property System will look into lower numbered data sets for the parameters, but not into higher numbered data sets. This is designed for convenience, to allow you to create a second data set which modifies only a few parameters, but you should be aware of this behavior. If you do not want this kind of defaulting, you must specify all parameters in the second data set which are defined in the first data set.

There are a few pre-defined property methods which use data set 2: NRTL-2, UNIQ-2, VANL-2, and WILS-2. When you add one of these property methods to your simulation, the binary parameter form for the data set it uses is added under **Methods | Parameters**. Also, UNIF-LL is defined to use the second data set of the UNIFAC parameters for liquid-liquid calculations. You can use data set 3 or higher for additional data sets for UNIFAC or with UNIF-LL. However, when using additional data sets with UNIF-LL, binary group parameters will not be retrieved from the built-in parameter table; you must specify the binary group parameters for all group-group pairs relevant to your model.

Note: Data regression runs can only manipulate the first data set. You can copy parameters obtained through data regression into any other data set and then use that data set during simulation runs.

Modifying and Creating Routes

The built in routes in the Aspen Physical Property System cover most engineering needs (see Routes and Models). However, while modifying or creating property methods you may need a route that is not built in (see Modifying and Creating Property Methods). You can create such a route based on the available methods. This section explains and gives examples of modifying and creating routes.

To decide if you want to create a new route or modify an existing route, apply the same reasoning as for deciding whether to modify or create a new property method (see Creating New Property Methods). We recommend you choose a new route ID.

To modify an existing route or create a new route:

1. Follow the procedure to trace routes, and consider the available methods for the property of interest. Decide on the route you want to modify, or the method you want to use to create a route. When you are modifying routes, start at the highest routes in the tree to be modified, since modifying these routes may change the subordinate routes used. Revisit this step after modifying a route.
2. In the navigation pane, open **Methods**, then click **Routes**.

   The **Routes** Object Manager appears. There are no objects listed because there are hundreds of available routes. So you need to know from the analysis you did on the **Selected Methods | Routes** sheet which route you want to modify.
3. Click **New**. Enter a new route ID to create a new route, or enter an existing route ID to modify an existing route.

   The **Routes | Specifications** sheet appears. At the top are the:
   - Property name
   - Method code (described in Methods earlier in this chapter)
   - Route ID of the route to modify
4. When you base your new route on an existing route, enter the property name in the **Property** name field and the base route ID in the **Copy route from** field, and make your changes.

   Or

   When you create a completely new route, enter the property name and method code. Fill the **Route ID** and **Model name** fields.
5. Use the **Selected Methods | Routes** sheet and enter the new route in a property method.

   Or

   Use the **Routes | Specifications** sheet of another route to use the newly created route in another route.

Example 1 describes how to use a second data set of NRTL parameters for HLXS. Example 2 describes how to use your own model for the liquid enthalpy.

Example 1: Use a second data set of NRTL parameters

The representation of two properties with one data set is sometimes not satisfactory, for example with VLE and excess enthalpy data. If two data sets can describe the properties separately, you will need to use both sets in the calculation.

In this example, one set of binary parameters for the NRTL model is used for VLE calculations. A second set of binary parameters is used for excess enthalpy (HLXS).

Create a new route to calculate HLXS. The simplest way is to modify the existing route used in the NRTL property method. The Route ID is HLXS10. On the **Methods | Routes | Specification** sheet, change **Data Set** from 1 to 2.

Example 2: Using your own model for the liquid enthalpy

Your company has developed a correlation for the enthalpy in a specific process stream that you want to use. The necessary user model subroutines have been written according to *Aspen Plus User Models*. All built in routes in the Aspen Physical Property System for the liquid molar enthalpy are based on methods 2, 3 or 4. However, to use the user model, method 1 (Specified model) is needed. Because no existing route uses method 1 or needs this type of model, there is no model for liquid enthalpy on the **Selected Methods | Models** sheet.

Create a new route, for example HLMXAP, using method 1. On the **Routes | Specifications** sheet. the property name HLMX appears in the Model area. Click the **Model** name field and select **HL2USR**, the liquid mixture enthalpy user model.

Reference the route HLMXAP in the property method on the **Selected Methods | Routes** sheet. You can check that the user enthalpy model HL2USR appears on the **Selected Methods | Models** sheet.

4 Electrolyte Calculation

Electrolyte process calculation has many applications. In the Aspen Physical Property System, you can analyze and optimize processes involving ionic species, complex ions, salt precipitation, with strong acids, weak acids and bases.

Examples of applications for electrolyte process calculation with the Aspen Physical Property System include:

- Sour water stripping (petrochemical industry)
- Caustic brine evaporation and crystallization (chlor-alkali industry)
- Acid gas removal (chemical and gas industries)
- Nitric acid separation (nuclear chemical industry)
- Trona processing (mining industry)
- Organic salt separation (biochemical industry)
- Black liquor evaporation (pulp and paper industry)

Electrolyte systems have three important characteristics:

- Solution chemistry in the liquid phase
- Apparent and true component compositions are different
- Non-ideal liquid phase thermodynamic behavior

This chapter describes applications of electrolyte process calculation and reviews the following fundamental characteristics of electrolyte systems:

- Solution chemistry
- Apparent component and true component approaches
- Aqueous electrolyte chemical equilibrium
- Electrolyte thermodynamics models
- Electrolyte data regression

Solution Chemistry

The solution chemistry involves a variety of chemical reactions in the liquid phase. Examples of such chemical reactions are:

- Complete dissociation of strong electrolytes
- Partial dissociation of weak electrolytes
- Ionic reactions among ionic species
- Complex ion formation
- Salt precipitation and dissolution

These chemical reactions occur rapidly in solution, so chemical equilibrium conditions are assumed.

Solution chemistry affects electrolyte process calculation by influencing physical properties, phase equilibrium, and other fundamental characteristics of electrolyte systems. For most nonelectrolyte systems, chemical reactions occur only in reactors. For electrolyte systems, chemical equilibrium calculations are essential to all types of unit operations modeling.

Solution chemistry dictates the true components in solution and imposes equality constraints on their composition. The chemical equilibrium relationship for reaction *j* is expressed as:

$$\ln K_j = \sum_i v_{i,j} \ln a_i \tag{1}$$

Where:

K_j = Chemical equilibrium constant
$v_{i,j}$ = Reaction stoichiometric coefficient of component *i*
a_i = Activity of component *i*

Computation of the solution chemistry is often combined with phase equilibrium calculations. Typical electrolyte calculations involving solution chemistry are:

- Liquid (aqueous) phase equilibrium (for example, calculating the pH for the titration of organic acid with caustic solution)
- Vapor-liquid (aqueous) phase equilibrium (for example, extractive distillation with salts as extractive agents, and sour water stripping)
- Liquid (aqueous)-liquid (organic) phase equilibrium (for example, hydrocarbon-sour water system and liquid-liquid extraction of metals)
- Liquid (aqueous)-solid equilibrium of salt precipitation (for example, crystallization of organic or inorganic salts)

To simulate an electrolyte system, you must properly identify all relevant chemical reactions. Physical interactions in solutions are sometimes described by postulating chemical reactions at equilibrium. The chemical theory of solutions is used only for real chemical reactions. Incorrect assumptions about the solution chemistry is the major cause of inaccuracies in calculations of reactive chemical systems.

Use the Electrolyte Expert System to identify all relevant chemical reactions. Starting from this set of reactions, you can remove and/or add reactions as required to properly represent your process.

You can use the **Chemistry** form to describe the solution chemistry and to enter the chemical equilibrium constants. However, we strongly recommend that you use the **Elec Wizard** on the **Components | Specifications | Selection** sheet and allow the Electrolyte Expert System to set up the property specifications for you.

For a system with a solvent dielectric constant less than 10, ionic reactions do not take place. Therefore, the Aspen Physical Property System bypasses all solution chemistry calculations for such systems.

If you define the reactions on the **Chemistry** form, the Aspen Physical Property System checks for infeasible or redundant reactions. If such reactions exist, the Aspen Physical Property System ignores them during the calculations.

Apparent Component and True Component Approaches

As a result of the solution chemistry, a set of true species is present in the liquid phase that differs from apparent molecular components. Apparent or parent components are present in the system if no reactions occurred. For example, the sour water stripper system has three apparent molecular components: water, ammonia, and hydrogen sulfide. The three molecular components dissociate in the liquid phase.

There are four ionic reactions:

$$2H_2O \quad \leftrightarrow \quad H_3O^+ + OH^- \tag{2}$$

$$NH_3 + H_2O \quad \leftrightarrow \quad NH_4^+ + OH^- \tag{3}$$

$$H_2S + H_2O \quad \leftrightarrow \quad H_3O^+ + HS^- \tag{4}$$

$$HS^- + H_2O \quad \leftrightarrow \quad H_3O^+ + S^{-2} \tag{5}$$

Five ionic species are thereby produced from these aqueous phase ionic reactions. All components in these reactions exist at chemical equilibrium conditions and are the true components of the electrolyte system. The apparent components are H_2O, NH_3, and H_2S.

These two sets of components have major effects on the treatment of electrolyte process calculation. Apparent components are of major concern to some electrolyte processes since process measurements are usually expressed in terms of apparent components. To other electrolyte processes, expression in terms of true species is the only way to characterize an electrolyte system. The selection of apparent components or true components therefore depends on the type of electrolyte system you simulate.

Three types of molecular components may be present in an electrolyte system: solvents, molecular solutes, and electrolytes. As a result of electrolyte solution chemistry, ions, salts, and nonvolatile molecular solutes may be present as additional true species. These components are defined as:

- Solvent: water is the solvent for aqueous electolyte systems. For mixed-solvent electrolyte systems, there are other solvent components in addition to water.
- Molecular solutes are molecular species, other than solvent compounds, that exist in the liquid phase in molecular form. All molecular solutes are treated with Henry's law. They are often supercritical components.
- Electrolytes are also molecular species. However, strong electrolytes dissociate completely to ionic species in the liquid phase. Undissociated weak electrolytes can be solvent components or molecular solutes.
- Ions are nonvolatile ionic species that exist only in the liquid phase.
- Salts are nonvolatile molecular species that exist as solids.

Choosing the True or Apparent Approach

The apparent component approach and the true component approach are interchangeable because liquid solution chemistry based on apparent component composition defines the true component composition of a system. The Aspen Physical Property System calculates thermodynamic properties of components and mixtures expressed in terms of apparent component composition from properties expressed in terms of true component composition. For example, the liquid fugacity coefficient of ammonia with the apparent component approach is calculated from the liquid fugacity coefficient of ammonia with the true component approach:

$$\varphi_i^{a,l} = \varphi_i^{t,l} \frac{x_i^t}{x_i^a} \tag{6}$$

Where:

$\varphi_i^{a,l}$ = Fugacity coefficient of apparent component *i*

$\varphi_i^{t,l}$ = Fugacity coefficient of true component *i*

x_i = Liquid component mole fraction of component *i* (superscript *a* indicates apparent composition, *t* indicates true composition)

Similar relationships are established for other properties (Chen et al., 1983). However, the apparent component mole fractions are not always calculated from the true component mole fractions because ambiguity can exist in the stoichiometric relations. This leads to a limitation in calculating the mixture heat capacity (CPMX) in true component systems, because it is calculated numerically from enthalpy calculations at different temperatures. The calculation accounts for this by calculating compositions at different temperatures and enthalpies based on those compositions and temperatures, which is only an approximation of the effect of composition change, and this approximation may be slightly different in true and apparent approach. The enthalpy, Gibbs free energy, entropy, and most other mixture properties should be the same whether true or apparent component approach is used, within the limitations of the true and apparent component approaches described below.

Using the apparent component approach in vapor-liquid equilibrium implies:

- The vapor-liquid equilibrium is solved in terms of apparent components only.
- The liquid solution chemistry in the liquid is solved in terms of true and apparent components.

This approach restricts the specification of the solution chemistry, because the reaction products (which are true components only by definition) cannot contain volatile components. Only apparent components can take part in vapor-liquid equilibrium. The true component approach does not have this restriction.

Note: True and apparent component approaches only apply to the liquid phase. The vapor phase does not contain ions, so this distinction is meaningless there.

In process calculation, the true component approach requires that you specify the process in terms of true components. The Aspen Physical Property System carries true components and their compositions in each process stream and each unit operation. Unit operation computational algorithms have been developed to solve the chemical equilibrium relationship in addition to the unit-operation describing equations.

The apparent component approach requires that you specify the process only in terms of apparent components. The solution chemistry and the true components are handled by the physical property system and are transparent to process flowsheets and unit operations.

The apparent component approach makes it possible to use existing unit operation computational algorithms, such as:

- Flash algorithms for vapor-liquid equilibrium
- Liquid phase splitting algorithms for liquid-liquid equilibrium
- Distillation algorithms

Rigorous representation of the (effective) partial molar properties of apparent components requires the solution of the chemical equilibrium and the knowledge of the partial molar properties of the true components.

Deciding whether to use the apparent component or true component approach can depend on:

- Your personal preference
- The way you specify the process (in terms of apparent components or true components)
- Convergence considerations

Note: While true and apparent approaches generally produce the same results, there are certain issues to be aware of with true-species electrolyte problems:

- Certain unit operation models do not support true species electrolyte chemistry. These models are DSTWU, Distl, SCFrac, MultiFrac, PetroFrac, BatchSep, Extract, REquil, RGibbs, and RBatch. In addition, the solids models do not support salt formation within the block from true species electrolytes (though the liquid compositions will be resolved), except for Crystallizer when using the option that salt precipitation is calculated from the chemistry. RPlug and RCSTR can be used with true species electrolyte chemistry provided that the reactions in the Reactions object do not contain electrolytic equilibrium reactions (such as $H_2O \Leftrightarrow H^+ + OH^-$) and no species participates in both reactions and chemistry.
- In true species electrolyte systems, the heat capacity cannot be calculated precisely. The heat capacity is calculated as a numerical derivative of the enthalpy using temperatures near the temperature of the system. However, in electrolyte systems, the true composition can vary by a meaningful amount even with small changes in temperature. In both true and apparent approaches, the true composition is calculated separately at each temperature, so an approximation of this effect is included in the heat capacity calculation. This issue does not affect any other properties or the model results (other than calculated heat capacity).
- In true species problems, it is possible to specify feed streams with ions. If you do so, you should specify the stream in mole basis. Specifying ion concentrations in mass basis will lead to rounding errors in the charge balance, which can cause the whole problem to be out of charge balance.
- In true species problems, using a Design Spec to manipulate the flow rate of an electrolyte component does not work as you might think. You should either manipulate the flow rate of a stream of that pure component which is subsequently mixed to produce the desired feed, or use the apparent component approach instead. For details, see Troubleshooting Design Specifications in the help.

Generally, the apparent component approach is preferred for simple electrolyte systems. It offers the advantage that only apparent components need to be considered. When the system grows more complex and it becomes difficult to select the apparent components, the true component approach is preferred. For complex distillation columns or flowsheet specifications, the true component approach can improve convergence.

Important: When the apparent components yield volatile reaction products, always use the true component approach.

When you use apparent components, the Aspen Physical Property System checks for generation of volatile species in excess of an amount determined by a tolerance, and generates an error if such a problem is found. You can adjust the tolerance or disable the check using the **Setup | Calculation Options | Reactions** sheet, but the recommended way to resolve this error is to use the true component approach.

Note: When salts are precipitating in two-liquid solutions, the salts may appear with either liquid phase. This is of importance in the apparent component approach where those salts are not differentiated from the rest of the electrolyte, possibly leading to multiple solutions based on initial solution state or convergence options. However, the multiple solutions in this case represent the same true-species composition. Only when the two liquid phases are separated into separate streams by an operation such as Flash3 or Decanter is there a real problem; to avoid this problem, use the true component approach.

If you use the apparent component approach, solution chemistry is required.

Reference

C.C. Chen, H.I. Britt, J.F. Boston, and W.M. Clarke, "Thermodynamic Property Evaluation in Computer-Based Flowsheet Simulation for Aqueous Electrolyte Systems," Paper presented at the Denver AIChE Meeting, August, 1983.

Reconstitution of Apparent Component Mole Fractions

Several electrolyte property models in the Aspen Physical Property System use the technique of constructing a set of arbitrary mole fractions of all possible apparent components from a mixture described in terms of compositions of true components. These models are listed in the following table, and are discussed in detail in *Physical Property Models*.

Model Name	**Property**
Clarke Aqueous Electrolyte Volume	Molar volume
Jones-Dole	Viscosity
Riedel	Thermal conductivity
Nernst-Hartley	Diffusivity
Onsager-Samaras	Surface tension

The mole fractions of the apparent components are reconstituted from mole fractions of true components, even if you use the apparent component approach. All possible apparent components *ca* from cations *c* and anions *a* are considered. For example, if you dissolve calcium sulphate and sodium chloride in water, then the solution contains: Na^+, Ca^{2+}, SO_4^{2-}, and Cl^-. This solution could have been made from water and an infinite number of different combinations of amounts of the apparent components $CaSO_4$, $CaCl_2$, NaCl, and Na_2SO_4.

From all possible solutions, the Aspen Physical Property System uses one arbitrary solution of the amounts of apparent electrolytes:

$$n_{ca}^{a} = \frac{n_c^t n_a^t}{\sum_c z_c n_c^t} \tag{7}$$

This solution generates all possible combinations of anions and cations. However, for the case of 2-2 electrolytes, the amount is multiplied by 2, to avoid the creation of, for example, $Ca_2(SO_4)_2$ instead of $CaSO_4$. In general, the correction factor should be the highest common factor of the charges (z_c) and (z_a), but the 3-3 or 2-4 electrolytes are not known.

From this the total amount of apparent moles and apparent mole fractions can be calculated:

$$x_k^a = \frac{n_k^a}{n_{tot}^a} \tag{8}$$

Where *k* can refer to any solvent *B*, molecular solute *i*, or apparent electrolyte *ca*.

Aqueous Electrolyte Chemical Equilibrium

In determining the composition of an electrolyte system, it is important to know the equilibrium constants of the reactions taking place. An equilibrium constant is expressed as the product of the activity of each species raised to its stoichiometric coefficients. Two different scales for equilibrium constants are used in the Aspen Physical Property System, the molality scale and the mole fraction scale.

The Mole Fraction Scale

The equilibrium constant is written as follows:

$$K = (x_w \gamma_w)^{v_w} \prod_{i \neq w} (x_i \gamma_i^*)^{v_i} \tag{1}$$

or

$$\ln K = v_w \ln(x_w \gamma_w) + \sum_{i \neq w} v_i (x_i \gamma_i^*) \tag{2}$$

Where:

K = Equilibrium constant

x_w = Water mole fraction

γ_w = Water activity coefficient

x_i = Mole fraction of non-water component (solute)

γ_i = Activity coefficient of non-water component (solute)

v_i = Stoichiometric coefficient

The Molality Scale

The equilibrium constant is written as follows:

$$K_m = (x_w \gamma_w)^{v_w} \prod_{i \neq w} (m_i \gamma^*_{m,i})^{v_i} \tag{3}$$

or

$$\ln K_m = v_w \ln(x_w \gamma_w) + \sum_{i \neq w} v_i (m_i \gamma^*_{m,i}) \tag{4}$$

Where:

K_m = Equilibrium constant on molality scale

m_i = Molality of non-water component (solute)

$\gamma_{m,i}$ = Activity coefficient of non-water component (solute) on molality scale

The activity coefficient of non-water component (solute) on the molality scale is defined as follows:

$$m_i \gamma^*_{m,i} = x_i \gamma^*_i \left(\frac{1000}{M_w} \right) \tag{5}$$

Where:

M_w = Molecular weight of water

Using equation 5, we can convert the logarithm of the equilibrium constant from the mole fraction scale to the molality scale:

$$\ln K_m = \ln K + \sum_{i \neq w} v_i \ln\left(\frac{m_i \gamma^*_{m,i}}{x_i r^*_i} \right) = \ln K + \ln\left(\frac{1000}{M_w} \right) \sum_{i \neq w} v_i \tag{6}$$

This derivation is general and is not tied to a particular activity coefficient model, even though the activity coefficients γ_w and γ_i* have to be calculated from a model or correlation.

Example

For the reaction:

$$NaCl \leftrightarrow Na^{+} + Cl^{-} \tag{7}$$

The equilibrium constant is:

$$K = \frac{a_{Na^{+}} . a_{Cl^{-}}}{a_{NaCl}} \tag{8}$$

Where *a* is the activity of a species. Therefore, we have:

$$v_{Na^{+}} = v_{Cl^{-}} = 1, \qquad v_{NaCl} = -1 \tag{9}$$

$$\sum_{i \neq w} v_i = v_{Na^{+}} + v_{Cl^{-}} + v_{NaCl} = 1 \tag{10}$$

$$\ln K_m = \ln K + \ln\left(\frac{1000}{M_w}\right) \tag{11}$$

Equation 11 holds for all 1-1 aqueous electrolytes.

The molality scale equilibrium constant is usually expressed in the form:

$$\ln K_m = a + (b/T) + (c \times \ln T) + (d \times T) \tag{12}$$

Combining equations 11 and 12, we can calculate the equilibrium constant in either scale.

If chemical equilibrium constants are not available, the Aspen Physical Property System estimates them from the reference state free energy of the system:

$$\ln K = \frac{\Delta G_m^{*}}{RT} \tag{13}$$

Applying equation 13 to 1-1 electrolyte systems using equation 11:

$$\ln K_m = \frac{\Delta G_m^{*}}{RT} + \ln\left(\frac{1000}{M_w}\right) \tag{14}$$

More generally, we can rewrite equation 14 as follows:

$$\ln K_m = \frac{\Delta G_m^{*}}{RT} + \ln\left(\frac{1000}{M_w}\right) \sum_{i \neq w} v_i \tag{15}$$

The Aspen Physical Property System offers a number of methods for calculating ΔG_m^{*}, including Electrolyte NRTL.

Electrolyte Thermodynamic Models

In electrolyte process calculation, the following thermophysical properties must be computed at a given temperature, pressure and composition:

- Activity coefficient
- Enthalpy
- Reference state Gibbs energy

These properties are necessary to perform phase equilibrium, chemical equilibrium, and mass and energy balance calculations. Activity coefficients are the most critical properties for process calculation. They determine the flow rates, compositions, and stability of phases.

Advances in electrolyte thermodynamics have produced several semi-empirical excess Gibbs energy models that correlate and predict: activity coefficients of individual ions, mean ionic activity coefficients, and activity coefficients of molecular solvents and solutes. The Pitzer equation, the Electrolyte NRTL Model, and the Zemaitis equations are the most widely adopted equations among these models.

Pitzer Equation

The Pitzer equation is a virial expansion equation. The model requires second-order parameters at low concentrations, and both second- and third-order parameters at high concentrations. The equation has been applied successfully to represent data within experimental error from dilute solutions up to an ionic strength of six molal for both aqueous single strong electrolyte systems and multicomponent strong electrolyte systems (Pitzer, 1973). The Pitzer equation is also extended to model aqueous weak electrolyte systems (Chen et al., 1982). It provides a thermodynamically consistent model that accurately represents electrolyte nonideality for many industrial aqueous electrolyte systems.

This model is the basis for the PITZER property method. For details on the model, see Pitzer Activity Coefficient Model in *Physical Property Models*.

References

C.C. Chen, H.I. Britt, J.F Boston, and L.B. Evans, "Local Composition Model for Excess Gibbs Energy of Electrolyte Systems," *AIChE J.*, Vol. 28, (1982), p. 588.

Pitzer, K.S., "Thermodynamics of Electrolytes.I. Theoretical Basis and General Equations," *J. Phys. Chem.*, Vol. 77, (1973), p. 268.

Electrolyte NRTL Equation

The electrolyte NRTL equation provides another thermodynamically consistent model for aqueous electrolyte systems. This equation was developed with the local composition concept. This concept is similar to the NRTL (Non-Random Two Liquid) model for nonelectrolyte systems (Renon and Prausnitz, 1968). With only binary parameters, the equation satisfactorily represents physical interactions of true species in aqueous single electrolyte systems and multicomponent electrolyte systems over wide ranges of concentrations and temperatures. This model can represent infinitely dilute electrolyte systems (where it reduces to the Debye-Hückel model), nonelectrolyte systems (where it reduces to the NRTL model), and pure fused salts. It connects these limiting systems. The equation has been extended to model mixed solvent electrolyte-systems (Mock et al., 1984).

This model is the basis for the ELECNRTL property method. For details on the model, see Electrolyte NRTL Activity Coefficient Model in *Physical Property Models*.

References

B. Mock, L.B. Evans, and C.-C. Chen, "Phase Equilibria in Multiple-Solvent Electrolyte Systems: A New Thermodynamic Model," Paper presented at the Boston Summer Computer Simulation Conference, July 1984.

H. Renon and J.M. Prausnitz, "Local Compositions in Thermodynamic Excess Function for Liquid Mixtures," *AIChE J.*, Vol. 14, (1968), p. 135.

Zemaitis Equation (Bromley-Pitzer Model)

The Zemaitis equation is based on the Bronsted-Guggenheim mean ionic activity coefficient equation with the Guggenheim β term expressed in Bromley's form as an expansion of ionic strength. The activity of solvent water in single electrolyte systems is then computed by application of the Gibbs-Duhem integration on the mean ionic activity coefficient equation. In multicomponent electrolyte systems, the activity coefficient of solvent water is computed with the Meissner approximation to avoid excessive Gibbs-Duhem integration (Bromley, 1973). Activity coefficients of molecular solutes are estimated with the Setschenow equation. The Zemaitis equation is not a thermodynamically consistent model, and binary parameters are empirical functions of ionic strength. The model offers the advantage of predicting mean ionic activity coefficients for unmeasured electrolyte systems from Bromley's correlation of binary parameters (Meissner and Kusik, 1973). For details on the model, see Bromley-Pitzer Activity Coefficient Model in *Physical Property Models*.

References

L.A. Bromley, "Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions," *AIChE J.*, Vol. 18, (1973), p. 313.

H.P. Meissner and C.L. Kusik, "Aqueous Solutions of Two or More Strong Electrolytes-Vapor Pressures and Solubilities," *Ind. Eng. Chem. Process Res. Develop.*, Vol. 12, (1973), p. 205.

Electrolyte Data Regression

Data regression is a critical part of electrolyte process calculation. For example, electrolyte activity coefficient models require regression of experimental data to determine model parameters. It may also be necessary to determine chemical equilibrium constants by data regression.

The Aspen Physical Property System Data Regression System (DRS) can be used for electrolytes. There are two unique considerations for electrolyte systems:

- Ions are nonvolatile, so vapor-liquid phase equilibrium constraints for ions are not applicable.
- The chemical equilibrium constraint of the solution chemistry must be satisfied.

Experimental data for electrolyte systems can be divided into four main categories for both single electrolyte systems and multicomponent electrolyte systems:

- Electrolyte properties, such as mean ionic coefficients
- Molecular properties, such as osmotic coefficient, solvent vapor pressure, vapor-liquid phase equilibrium data, and liquid-liquid phase equilibrium data
- Solution properties, such as liquid mixture enthalpy and density
- Salt solubility

Electrolyte data regression is most often performed on electrolyte properties and molecular properties to determine activity coefficient model parameters. Solution enthalpy data provide valuable information on temperature derivatives of activity coefficients and can be used with other data to determine the temperature dependency of activity coefficient model parameters. These data can also be used to regress chemical equilibrium constants and activity coefficient model parameters. Salt saturation limits can be used to obtain equilibrium constants for salt precipitation (salt solubility product).

See Regressing Property Data in Using the Properties Environment in help for details on data regression.

5 Free-Water and Rigorous Three-Phase Calculations

This chapter describes free-water, dirty-water, and rigorous three-phase calculations in the Aspen Physical Property System. Guidelines to help you choose the most appropriate method are included.

The following table lists the unit operation models that allow three-phase calculations. The table shows, for each model, whether or not free-water, dirty-water, and/or rigorous three-phase calculations can be performed.

Unit Operation Models That Allow Three-Phase Calculations

Name	Description	Free-Water Calculations	Dirty-Water Calculations	Water Decant Stream	Rigorous 3-Phase Calculations
Mixer	Stream mixer	YES	YES	YES	YES
FSplit	Stream splitter	YES	YES	NO	YES
Sep	Component separator	YES	YES	NO	YES
Sep2	Two outlet separator	YES	YES	NO	YES
DSTWU	Shortcut distillation design	YES †	YES †	YES	NO
Distl	Shortcut distillation rating	YES †	YES †	YES	NO
SCFrac	Shortcut petroleum distillation	YES †	NO	YES	NO
RadFrac	Rigorous distillation	YES	YES	YES	YES
MultiFrac	Rigorous multicolumn distillation	YES	NO	YES	NO

Name	Description	Free-Water Calculations	Dirty-Water Calculations	Water Decant Stream	Rigorous 3-Phase Calculations
PetroFrac	Rigorous petroleum distillation	YES	NO	YES	NO
Extract	Rigorous liquid-liquid extractor	NO	NO	NO	††
Heater	Heater/cooler	YES	YES	YES	YES
Flash2	Two outlet flash	YES	YES	YES	YES
Flash3	Three outlet flash	NO	NO	NO	YES
Decanter	Liquid-liquid decanter	YES	NO	NO	††
Heatx	Two stream heat exchanger	YES	YES	YES	YES
MHeatx	Multistream heat exchanger	YES	YES	YES	YES
RStoic	Stoichiometric reactor	YES	YES	YES	YES
RYield	Yield reactor	YES	YES	YES	YES
RGibbs	Equilibrium reactor Gibbs energy minimization	NO	NO	NO	YES †††
Pump	Pump/hydraulic turbine	YES	YES	YES	YES
Compr	Compressor/turbine	YES	YES	YES	YES
MCompr	Multistage compressor/turbine	YES	YES	YES	YES
Crystallizer	Crystallizer	NO	NO	NO	NO
Pipeline	Pipeline	YES	NO	NO	YES
Dupl	Stream duplicator	—	—	—	—
Mult	Stream multiplier	—	—	—	—

†Condenser only

††Rigorous liquid-liquid equilibrium calculations

†††RGibbs handles any number of phases rigorously.

Free-Water and Dirty-Water Immiscibility Simplification

The unit operation models in the table labeled Unit Operation Models That Allow Three-Phase Calculations can handle the presence and the decanting of free water or dirty water, when performing flash calculations or liquid-liquid equilibrium calculations on water-organic systems in which the water phase is essentially pure or has trace amounts of organic components.

Free-water calculations involve special methods for calculating the solubility of water in the organic phase and a test for the presence of a pure water phase. Free-water calculations are always faster than rigorous three-phase calculations and require minimal physical property data preparation. Just like free-water calculations, dirty-water calculations also involve special methods for calculating the solubility of water in the organic phase. In addition to this, special methods are used to compute the solubility of organic compounds in the water phase.

For water-hydrocarbon systems, free-water calculations are normally adequate. The hydrocarbon solubility in the water phase is generally negligible. In applications where the hydrocarbon solubility in the water phase is of great concern (such as in an environmental study), use dirty-water or rigorous three-phase calculations.

For chemical systems such as water-higher alcohols, free-water or dirty-water calculations do not apply. Solubility of the organics in the water phase is significant. Rigorous three-phase calculations are required.

When you use the free-water or dirty-water calculation method, if a stream contains only water, all properties for the stream are calculated using the free-water method as if it was the main property method.

The assumptions of the free-water and dirty-water models preclude the use of electrolytes. If you have electrolytes in a two-liquid system, you should use the fully rigorous liquid-liquid models.

Specifying Free-Water or Dirty-Water Calculations

The free-water or dirty-water calculations are completely rigorous, except for the assumption that the water phase is pure or has only a trace amount of organic components. If free water or dirty water is present and you specify a decant stream for the block, the Aspen Physical Property System places the water phase in the decant stream. If you do not specify a decant stream, the Aspen Physical Property System mixes the water phase with the organic phase.

To request free-water or dirty-water calculations for	Use the Free-Water field to Yes or Dirty on the
The entire flowsheet	Setup Specifications Global sheet
An individual unit operation block	Block Options form for the block
An individual outlet stream in some blocks	Flash-Specs form for the block

For all unit operation blocks except the distillation models, you can select two types of free-water calculations using the following flash specification:

- Valid Phases=Vapor-Liquid, to consider vapor and liquid phases
- Valid Phases=Liquid-Only, to consider only liquid phases

Valid Phases=Vapor-Liquid-Liquid is reserved for rigorous three-phase calculations. If you specify Valid Phases=Vapor-Liquid-Liquid, any free-water specification is ignored. Dirty-water calculations will override the rigorous three-phase calculations.

For all distillation models except RadFrac, MultiFrac, and PetroFrac, free water calculations are performed in the condenser only. For RadFrac, MultiFrac, and PetroFrac, you can request free-water calculations for additional stages in the column. For details, please see MultiFrac in the help. Dirty-water calculations are allowed only in RadFrac and in the condenser of DSTWU and Distl.

Free-Water Phase Properties

The free-water phase K-value, K_w^*, is calculated as follows:

$$K_w^* = \varphi_w^{*,l} / \varphi_w^v$$

Where:

$\varphi_w^{*,l}$ = The fugacity coefficient of pure liquid water, calculated using a free-water property method (for example, the STEAM-TA property method)

φ_w^v = The fugacity coefficient of water in the vapor phase mixture, calculated using the primary property method

When a free-water phase is present, its other thermodynamic properties (such as enthalpy) and transport properties (such as viscosity) are calculated using the free-water property method.

Organic Phase Properties

The K-value of water in the organic phase (for both free-water and dirty-water calculations) is:

$$K_w^* = \gamma_w \varphi_w^{*,l} / \varphi_w^v$$

Where:

γ_w = The activity coefficient of water in the organic phase

$\varphi_w^{*,l}$ = The fugacity coefficient of pure liquid water, calculated using the free-water property method

φ_w^v = The fugacity coefficient of water in the vapor phase mixture, calculated using the primary property method

You can select the calculation methods for γ_w and φ_w^v using the Water solubility field on the **Methods | Specifications | Global** sheet or the **Block Options** form.

Note: These methods apply to all vapor-liquid calculations for activity and fugacity of water, whether or not free-water is specified, except in equation-oriented modeling, where it only applies to the free-water phase.

Water solubility option	**Calculate γ_w from**	**Calculate φ_w^v from**
0	$\gamma_w = \frac{1}{x_w^{sol}}$	Free-water property method
1	$\gamma_w = \frac{1}{x_w^{sol}}$	Primary property method
2	$\gamma_w = f(T, x_w)$ where $\gamma_w = \frac{1}{x_w^{sol}}$ when $x_w = x_w^{sol}$	Primary property method
3	Primary property method	Primary property method
4	$\gamma_w = 1$	Primary property method
5	$\gamma_w = f(T, x_w)$ where $\gamma_w = \frac{1}{x_w^{sol}}$ when $x_w = x_w^{sol}$	Free-water property method

Note: This should be left at the default value of **3** except when modeling water-hydrocarbon systems where two liquid phases form and the aqueous phase is almost pure water, and is modeled using the **Vapor-Liquid-Free Water** or **Liquid-Free Water** valid phases options.

Water solubility option 3 is not recommended for free-water systems unless binary interaction parameters regressed from liquid-liquid equilibrium data are available.

The limiting solubility of water in the organic phase (x_w^{sol}) is calculated as a mole fraction weighted average of the solubilities of water in the individual organic species:

$$x_w^{sol} = \frac{a}{1+a}$$

$$a = \sum_i x_i \frac{x_{wi}^{sol}}{1 - x_{wi}^{sol}}$$

Where:

x_i = Water-free mole fraction of the *i*th organic species

x_{wi}^{sol} = Mole fraction solubility of water in the *i*th species

The value of x_{wi}^{sol} is calculated as a function of temperature, using the Water Solubility model (WATSOL).

Dirty-Water Phase Properties

The K-value of water in the dirty-water phase, K_w^*, is calculated as follows:

$$K_w^* = \varphi_w^{*,l} / \varphi_w^v$$

Where:

$\varphi_w^{*,l}$ = The fugacity coefficient of pure liquid water, calculated using a free-water property method (for example, the STEAM-TA property method)

φ_w^v = The fugacity coefficient of water in the vapor phase mixture, calculated using the primary property method

The K-values of other components are calculated as follows:

$$K_i = \frac{\gamma_i \varphi_i^l}{\varphi_i^v}$$

Where:

$$\gamma_i = \frac{1}{x_i^{sol}}$$

x_i^{sol}, the solubility of component *i* in water, is calculated using the Hydrocarbon Solubility model (HCSOL).

Rigorous Three-Phase Calculations

The unit operation models that can perform rigorous three-phase or two-liquid-phase calculations are indicated in the table labeled Unit Operation Models That Allow Three-Phase Calculations. These calculations make no assumptions about the nature of the two liquid phases. The Aspen Physical Property System uses the primary property method to calculate the K-values of all components in both liquid phases. The second liquid phase does not have to be aqueous. If the second liquid phase is aqueous, the solubility of organics in water is treated rigorously. To obtain correct three-phase results, you must use the appropriate binary parameters for the property model used in the property method.

Specify rigorous three-phase calculations at the individual block level, using the flash option Valid Phases=Vapor-Liquid-Liquid, except for Flash3. Flash3 has no flash options, since it performs only rigorous three-phase flashes.

Extract always performs rigorous two-liquid-phase calculations.

6 Petroleum Components Characterization Methods

The Aspen Physical Property System provides a wide range of methods for characterization of petroleum fractions, or pseudocomponents. These methods are used to estimate parameters, such as critical temperature, and properties, such as ideal gas heat capacity, vapor pressure, and liquid viscosity. The following table lists the:

- Parameters that the Aspen Physical Property System estimates for petroleum fractions
- Methods available for each parameter. The literature references for each method are listed at the end of this chapter.

Petroleum Fractions Characterization Methods

Parameter	Description	Methods Available
MW	Molecular weight	Brule et al. (1982) Extended API (2002) Extended Twu (2002) Hariu-Sage (1969) Hariu-Sage-Aspen (1994) Kesler-Lee (1976) Riazi API (1986) Riazi API (1986), heavy petro Riazi-Daubert (1980) Tsang-Aspen (1978) User routine PCMWU Winn correlation (1957)

Parameter	Description	Methods Available
TC	Critical temperature	Brule et al. (1982) Cavett (1962) Extended Twu 1 (2002) Extended Twu 2 (2002) Extended Cavett (2002) Kesler-Lee (1976) Riazi API (1986) Riazi-Daubert (1980) Robinson-Peng (1978) Tsang-Aspen (1978) Twu (1984) User routine PCTCU Winn correlation (1957)
PC	Critical pressure	Cavett (1962) Extended Edmister (2002)Extended Twu (2002) Kesler-Lee (1976) Riazi API (1986) Riazi-Daubert (1980) Robinson-Peng (1978) Tsang-Aspen (1978) Twu (1984) User routine PCPCU Winn correlation (1957)
VC	Critical volume	Brule et al. (1982) Edmister (1984) Extended Twu (2002) Lee-Kesler (1984) Riedel (1954) Twu (1984) User routine PCVCU
OMEGA	Acentric factor	Defining relation Edmister (1984) Extended Lee-Kesler (2002) Kesler-Lee (1976) Kesler-Lee-Aspen (1994) Robinson-Peng (1978) User routine PCOMGU Twu generalized correlation (1994) Aspen-Twu generalized correlation
PL	Vapor pressure	BK-10 (AspenTech implementation) Kesler-Lee (1980) Maxwell-Bonnell (1955) Tsang-SWAP (1978) User routine PCPLU

Parameter	Description	Methods Available
VL	Liquid molar volume	Cavett (1974) Rackett (Spencer and Danner, 1972) User routine PCVOLU
WATSOL	Water solubility in hydrocarbon	Aspen API Kerosene Hibbard-Schalla (API) User routine PCWSLU User routine PCWSLU2
HCSOL	Hydrocarbon solubility in water-rich phase	Aspen User routine PCHSLU
MUL	Liquid viscosity	Watson (1935) User routine PCMULU User routine PCMULU2
CPIG	Ideal gas heat capacity	API Hybrid Brule et al. (1982) Cavett (1962) Kesler-Lee (1976) Mathias-Monks (1982) Simplified Lee-Kesler Tsang-Aspen (1978) User routine PCCPGU
DHVL	Enthalpy of vaporization	Kistiakowsky (1923) Vetere (1973) User routine PCDHVU
DHFORM	Ideal gas heat of formation at 298.15 K	Default to zero Edmister (1988) †† Edmister-API (1988) †† Edmister-API97 (1988) †† User routine PCDHFU
DGFORM	Ideal gas Gibbs free energy of formation at 298.15 K	Default to zero Edmister (1988) †† Edmister-API97 (1988) †† User routine PCDGFU
RKSKBV	RKS binary interaction parameters †	API 1978 API 1987 User routine PCRKIU User routine PCRKIU2
BWRGMA	BWR orientation parameter	Brule et al. (1982) User routine PCBWRU

Parameter	Description	Methods Available
TCBWR	BWR critical temperature	Brule et al. (1982) User routine PCBWRU
VCBWR	BWR critical volume	Brule et al. (1982) User routine PCBWRU

† The RKS binary interaction parameters are estimated for each pseudocomponent in pairs with certain light gases which are present in the simulation. The 1978 method estimates parameters for pseudocomponentswith CO_2, CO, H_2S, N_2. The 1987 method estimates parameters for pseudocomponents with methane, CO_2, H_2S, N_2, and H_2, and sets the parameters for pseudocomponentswith CO to zero.

†† The Edmister methods use data for paraffin, naphthene, and aromatic content (sometimes called PNA analysis), but the implementations in the Aspen Physical Property System use an API correlation based on molecular weight, refractive index, liquid density, liquid viscosity, and specific gravity to determine these values, even if you have entered values for these properties of the pseudocomponents.

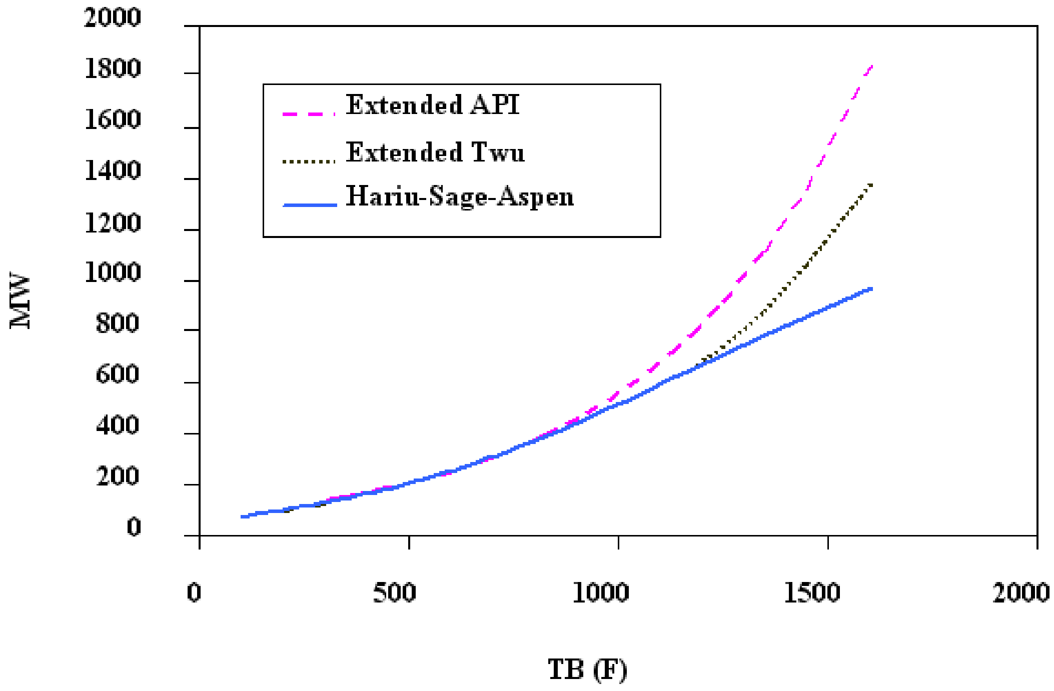
AspenTech Extensions to Characterization Methods for Petroleum Fractions

A number of the methods for characterization of petroleum fractions are AspenTech extensions to well-known methods. These are listed below. Plots are available showing how some of the extended methods compare for a typical crude assay.

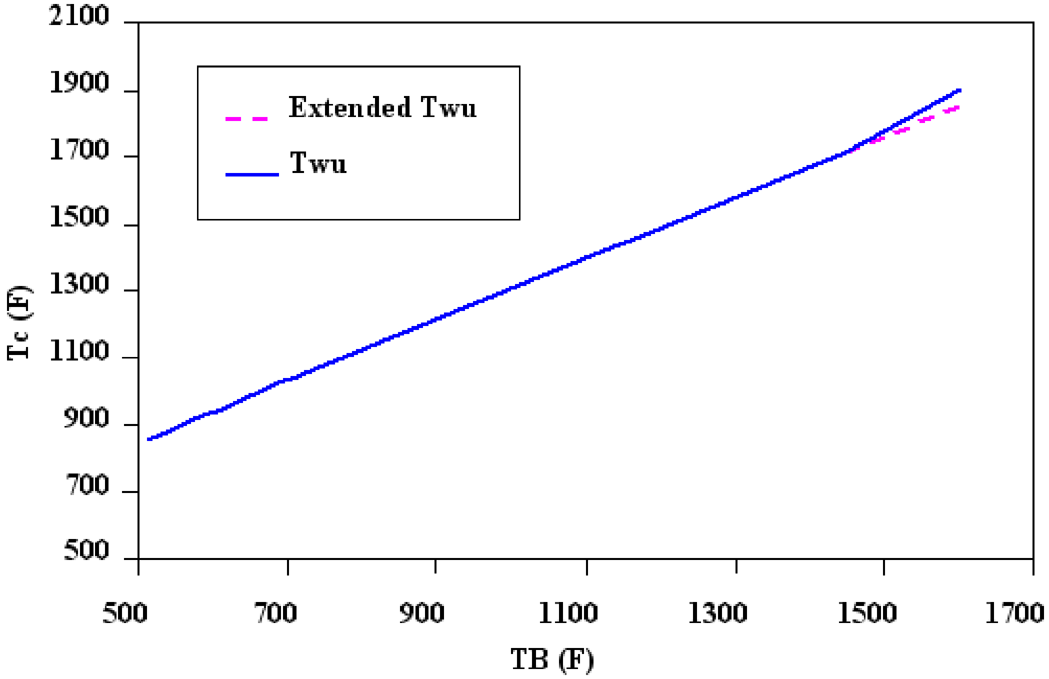
Property	Method	Description
Molecular weight	Hariu and Sage-Aspen	Hariu-Sage (1969) model with Aspen modification for light fractions.
	Extended API	Riazi-Daubert (1980) model with Aspen modification for light fractions.
	Extended Twu	Twu (1984) model with Aspen modification for high-boiling fractions.
Critical temperature	Extended Twu 1	Twu (1984) model with Aspen modification for high-boiling fractions using linear extrapolation.

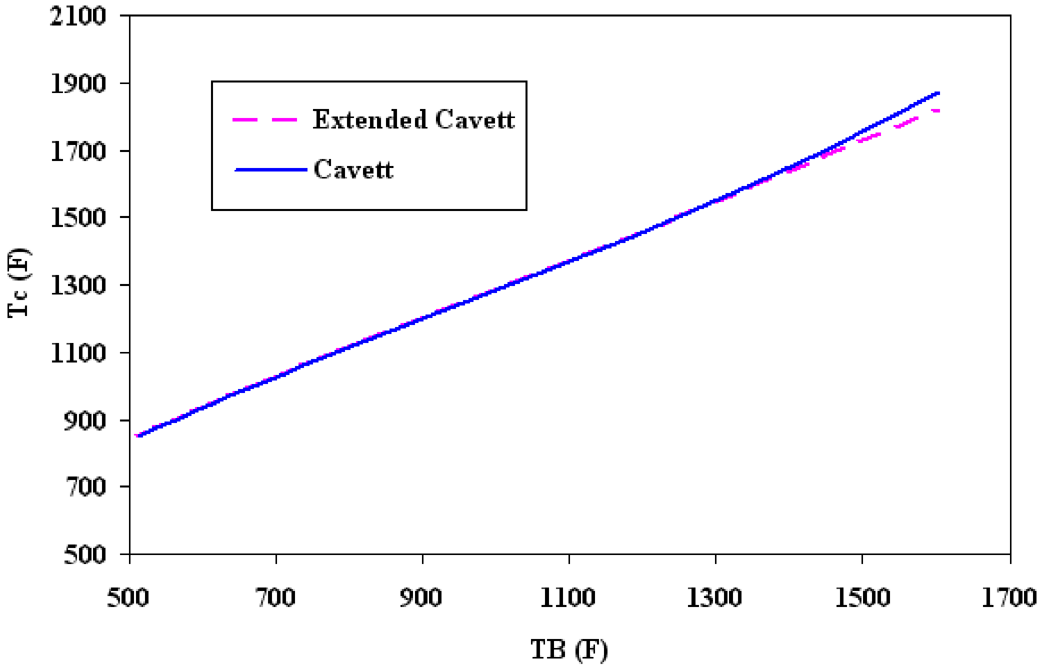
Property	Method	Description
	Extended Twu 1	Twu (1984) model with Aspen modification for high-boiling fractions using extrapolation based on constant Watson K.
	Extended Cavett	Cavett (1962) model with Aspen modification for high-boiling fractions.
Critical pressure	Extended Edmister	Edmister (1984) model with Aspen modification for high-boiling fractions.
	Extended Twu	Twu (1984) model with Aspen modification for high-boiling fractions.
Critical volume	Extended Twu	Twu (1984) model with Aspen modification for high-boiling fractions.
Acentric factor	Lee and Kesler, Aspen	Kesler-Lee (1976) model with Aspen modification for high-boiling fractions.
	Extended Lee-Kesler	Further modifications for high-boiling fractions.
	Aspen-Twu generalized correlation	Twu generalized correlation (1994) with Aspen improvement for heavy components.
Water solubility	Aspen	AspenTech empirical correlation
Ideal gas heat capacity	API Hybrid	Combination of API Technical databook procedure 7D4.2 and Brule et al. (1982)
	Simplified Lee-Kesler	Kesler-Lee (1976) model with AspenTech modification.

Comparison of Extended Molecular Weight Methods

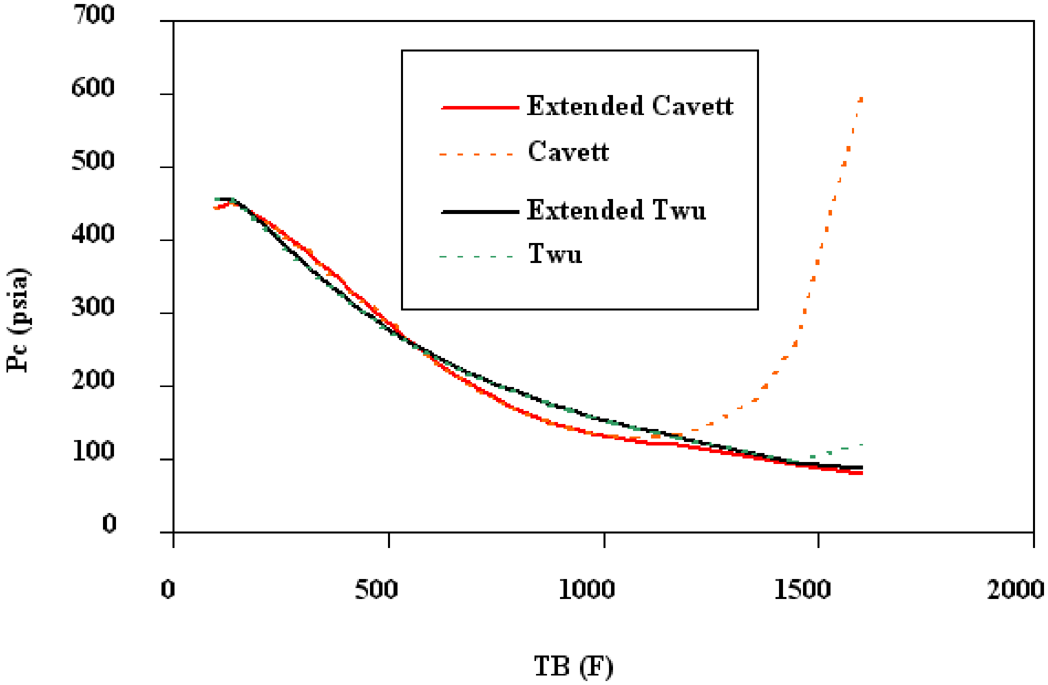


Comparison of Extended Critical Temperature Methods

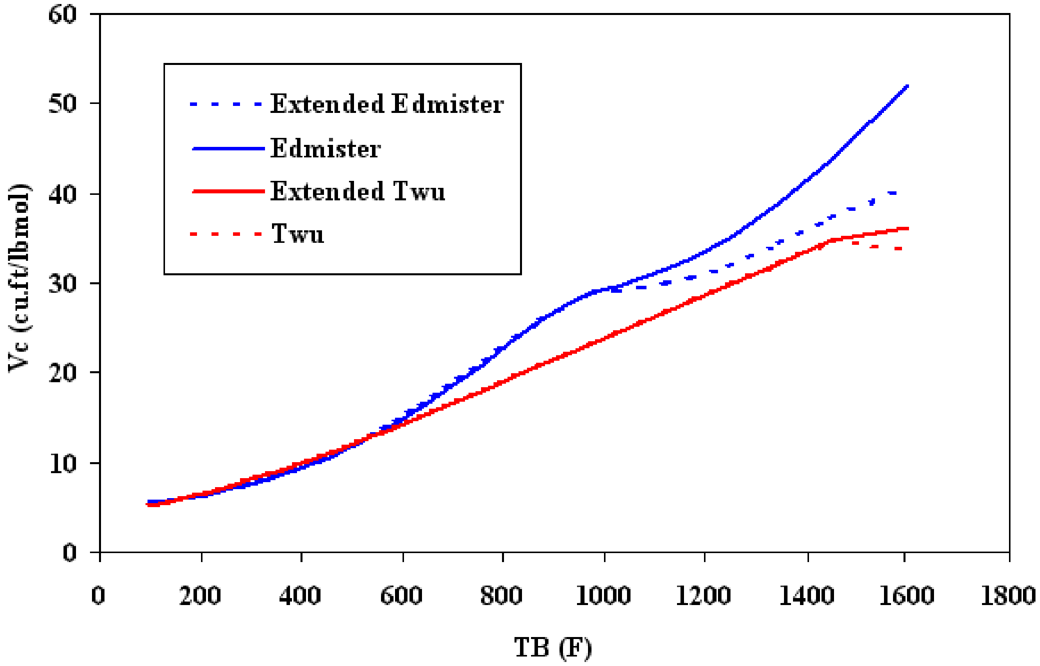




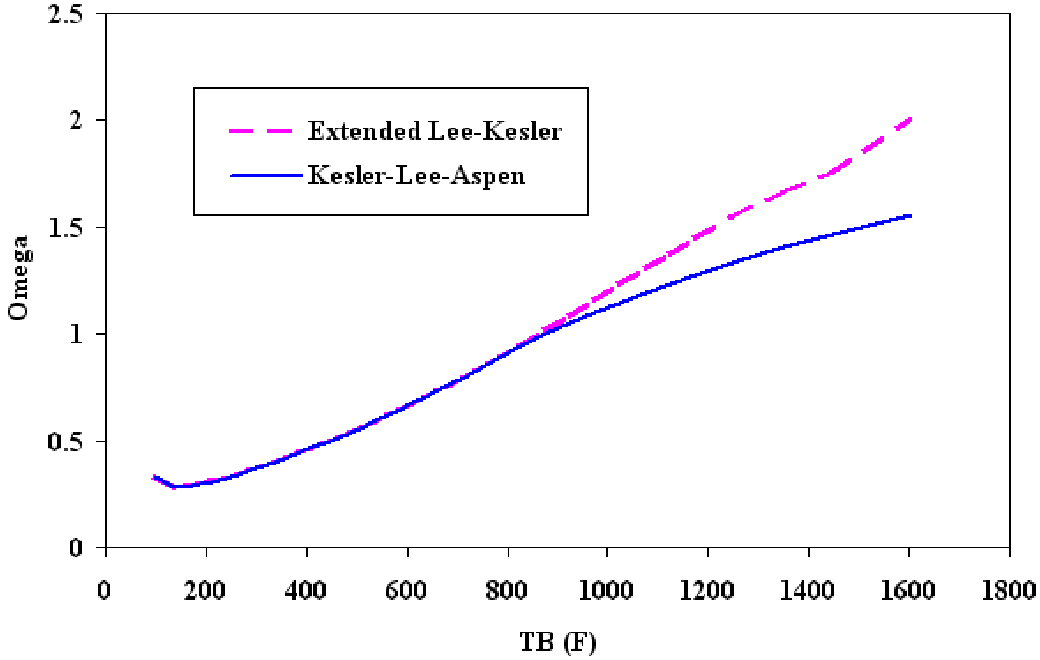
Comparison of Extended Critical Pressure Methods



Comparison of Extended Critical Volume Methods



Comparison of Extended Acentric Factor Methods



User Models for Characterization of Petroleum Fractions

All characterization parameters and properties of petroleum fractions can be estimated by user routines. See *Aspen Plus User Models*, Chapter 25, for details on writing these routines.

Property	**Routine**
Molecular weight	PCMWU
Critical temperature	PCTCU
Critical pressure	PCPCU
Critical volume	PCVCU
Acentric factor	PCOMGU
Vapor pressure	PCPLU
Liquid molar volume	PCVOLU
Water solubility	PCWSLU, PCWSLU2
Hydrocarbon solubility	PCHSLU
Liquid viscosity	PCMULU, PCMULU2
Ideal gas heat capacity	PCCPGU
Enthalpy of vaporization	PCDHVU
Standard enthalpy of formation	PCDHFU
Standard Gibbs free energy of formation	PCDGFU
RKS interaction parameters	PCRKIU, PCRKIU2
BWR orientation parameter, Tc, Vc	PCBWRU
Normal boiling point	PCABPU
Specific gravity	PCSGU

Property Methods for Characterization of Petroleum Fractions

Since there are several methods available for estimation of a given parameter, it is often difficult to select the appropriate method for the application. For your convenience, we have grouped several sets of methods into property methods. These selections are made according to standard industry practices, most commonly used methods, or based on AspenTech's own extensions. The AspenTech extensions are intended to improve the behavior of the correlations in the low and high-boiling ranges.

The following property methods are available:

- The API-METH property method consists of methods based mainly on the API procedure. This property method is appropriate for refinery applications.
- COAL-LIQ property method consists of methods developed for coal liquid applications. The database used to develop the correlations contains a large percentage of aromatic compounds.
- ASPEN property method consists of methods developed by AspenTech for petroleum components and methods based on the API procedure. This method is recommended.
- LK property method is based mainly on the methods of Kesler and Lee.
- API-TWU property method is based on the ASPEN property method, but uses the Twu correlations for critical properties.
- EXT-TWU property method is similar to the API-TWU method, except that AspenTech extensions to both low boiling and high boiling ranges are used for MW, TC, PC, VC, and acentric factor.
- EXT-API property method is similar to the EXT-TWU method, except that the extended API method is used for molecular weight and the extended Lee-Kesler method is used for acentric factor.
- EXT-CAV property method is similar to the EXT-API method, except that the extended Cavett method is used for critical temperature and the extended Edmister method is used for critical pressure and critical volume.

There are no documented temperature limits for these methods from their authors, but our studies show that the limits within which the methods are reliable depend on the property. The first five methods typically behave properly for fractions up to a normal boiling point of 800 to 1000 F. The extended methods extend the range of applicability for MW, TC, PC, and acentric factor to a normal boiling point of about 1500 F.

The models associated with each of the property methods available for characterization of pseudocomponents are listed in the tables below.

Property Method ASPEN: Aspen Tech and API procedures

Property	Model
Molecular weight	Hariu and Sage-Aspen
T_c	Riazi-Daubert
P_c	Riazi-Daubert
V_c	Riedel
Acentric factor	Lee and Kesler, Aspen
Vapor pressure	BK-10
Liquid molar volume	Rackett
Water solubility	Aspen
Liquid viscosity	Watson
Ideal gas heat capacity	Kesler-Lee
Enthalpy of vaporization	Vetere
Standard enthalpy of formation	Edmister
Standard Gibbs energy of formation	Edmister
RKS binary parameters	API 1978

Property Method API-METH: API Procedures

Property	Model
Molecular weight	Hariu-Sage
T_c	Riazi-Daubert
P_c	Riazi-Daubert
V_c	Riedel
Acentric factor	Kesler-Lee
Vapor pressure	Maxwell-Bonnell

Property	**Model**
Liquid molar volume	Rackett
Water solubility	Aspen
Liquid viscosity	Watson
Ideal gas heat capacity	Kesler-Lee
Enthalpy of vaporization	Vetere
Standard enthalpy of formation	Default to zero
Standard Gibbs energy of formation	Default to zero
RKS binary parameters	API 1978
BWR orientation parameter, T_c, V_c	Brule et al.

Property Method COAL-LIQ: for Coal Liquids

Property	**Model**
Molecular weight	Hariu-Sage
T_c	Tsang-Aspen
P_c	Tsang-Aspen
V_c	Riedel
Acentric factor	Kesler-Lee
Vapor pressure	Tsang-SWAP
Liquid molar volume	Rackett
Water solubility	Aspen
Liquid viscosity	Watson
Ideal gas heat capacity	Mathias-Monks
Enthalpy of vaporization	Vetere
Standard enthalpy of formation	Default to zero
Standard Gibbs energy of formation	Default to zero
RKS binary parameters	API 1978
BWR orientation parameter, T_c, V_c	Brule et al.

Property Method LK: Lee-Kesler

Property	Model
Molecular weight	Kesler-Lee
T_c	Kesler-Lee
P_c	Kesler-Lee
V_c	Riedel
Acentric factor	Kesler-Lee
Vapor pressure	Kesler-Lee
Liquid molar volume	Rackett
Water solubility	Aspen
Liquid viscosity	Watson
Ideal gas heat capacity	Kesler-Lee
Enthalpy of vaporization	Vetere
Standard enthalpy of formation	Edmister
Standard Gibbs energy of formation	Edmister
RKS binary parameters	API 1978

Property Method API-TWU: AspenTech, API, and Twu

Property	Model
Molecular weight	Hariu and Sage-Aspen
T_c	Twu
P_c	Twu
V_c	Twu
Acentric factor	Lee and Kesler, Aspen
Vapor pressure	BK-10
Liquid molar volume	Rackett
Water solubility	API kerosene-line
Liquid viscosity	Watson

Property	Model
Ideal gas heat capacity	Kesler-Lee
Enthalpy of vaporization	Vetere
Standard enthalpy of formation	Edmister
Standard Gibbs energy of formation	Edmister
RKS binary parameters	API 1978

Property Method EXT-TWU: Twu and AspenTech Extensions

Property	Model
Molecular weight	Extended Twu
T_c	Extended Twu
P_c	Extended Twu
V_c	Extended Twu
Acentric factor	Extended Twu
Vapor pressure	BK-10
Liquid molar volume	Rackett
Water solubility	API kerosene-line
Liquid viscosity	Watson
Ideal gas heat capacity	Kesler-Lee
Enthalpy of vaporization	Vetere
Standard enthalpy of formation	Edmister
Standard Gibbs energy of formation	Edmister
RKS binary parameters	API 1978

Property Method EXT-API: API, Twu, and AspenTech Extensions

Property	Model
Molecular weight	Extended API correlation

Property	Model
T_c	Extended Twu
P_c	Extended Twu
V_c	Extended Twu
Acentric factor	Extended Lee-Kesler
Vapor pressure	BK-10
Liquid molar volume	Rackett
Water solubility	API kerosene-line
Liquid viscosity	Watson
Ideal gas heat capacity	Kesler-Lee
Enthalpy of vaporization	Vetere
Standard enthalpy of formation	Edmister
Standard Gibbs energy of formation	Edmister
RKS binary parameters	API 1978

Property Method EXT-CAV: Cavett, API, and AspenTech Extensions

Property	Model
Molecular weight	Extended API correlation
T_c	Extended Cavett
P_c	Extended Edmister
V_c	Extended Edmister
Acentric factor	Extended Lee-Kesler
Vapor pressure	BK-10
Liquid molar volume	Rackett
Water solubility	Aspen
Liquid viscosity	Watson
Ideal gas heat capacity	Kesler-Lee
Enthalpy of vaporization	Vetere
Standard enthalpy of formation	Edmister

Property	Model
Standard Gibbs energy of formation	Edmister
RKS binary parameters	API 1978

Water Solubility in Petroleum Fractions

The solubility of water in the hydrocarbon phase is calculated by the water-solubility correlation. Coefficients for this correlation for a pseudocomponent can be calculated using any of the following:

- The Kerosene line correlation (API Technical databook procedure 9A1.4).
- An AspenTech proprietary correlation which depends on TB, SG and MW.
- The Hibbard & Schalla Correlation. API Technical Data Book Procedure 9A1.5

Estimation of NRTL and UNIQUAC Binary Parameters for Water and Petroleum Fractions

The NRTL and UNIQUAC binary parameters for water and pseudocomponents are intended for use in LLE calculations, as water and hydrocarbons tend to form two liquid phases. These interaction parameters are estimated from the mutual solubility data. The solubility of water is estimated from one of the methods described above. The solubility of pseudocomponent in water is estimated from the API procedure 9A2.17.

Since water and hydrocarbons are essentially immiscible, the mutual solubilities are very low. As a result, the solubility is inversely proportional to the infinite dilution activity coefficients. For infinitely dilute binary system, binary interaction parameters for the NRTL and UNIQUAC models can be computed directly from infinite-dilution activity coefficient data.

Estimation of ATOMNO and NOATOM for Petroleum Fractions

ATOMNO and NOATOM, which combine to form the chemical formula, are estimated from the molecular weight and carbon-to-hydrogen (C/H) ratio. The C/H ratio is estimated using the procedure in *Technical Data Book - Petroleum Refining*, vol. 2, fig. 2B6.1, American Petroleum Institute, 1983. These components are assumed to contain no atoms but carbon and hydrogen, and the carbon and hydrogen numbers are adjusted to meet the molecular weight and C/H ratio. As a result, H and C may be fractional.

Estimation of Flash Point

Aspen Plus provides several properties representing different methods of calculating the flash point for petroleum mixtures. The following methods are available:

- FLPT-API, the API method for determining flash point
- FLPT-PM, the Pennsky-Martens method (ASTM-D93)
- FLPT-TAG, the Tag method (ASTM-D56)

FLPT-API uses the ASTM D86 10% temperature for petroleum fractions or the normal boiling point for conventional components in a procedure based on the API computerized procedure 2B7.1 (Riazi, 1985, 1986). Linear extrapolation is also performed. The following correlation is used:

$$TFP = \frac{1}{-a + b/T10R + c\ln(T10R)}$$

Where

TFP = Flash point temperature in Rankine

T10R = D86 temperature at 10% volume, in Rankine

a, b, c = constants

The other two methods use a modified bubble point calculation described in Seader and Henley (1998). These methods use mole-weight-modified K-values for a bubble point flash in which the value of the summation $\sum K_i X_i$, normally 1, has been replaced with an experimentally determined parameter *a*. The parameter *a* has different values for the two methods.

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7 Property Parameter Estimation

This chapter describes:

- Estimation methods used by the Property Constant Estimation System (PCES)
- How to generate a report for the estimated parameters

If you request estimation, the Aspen Physical Property System, by default, estimates all missing property parameters required by physical property models. These parameters include any not available in the databank and not specified on Properties Parameters forms. The following table labeled Parameters Estimated by the Aspen Physical Property System lists all the parameters that the Aspen Physical Property System can estimate.

Parameters Estimated by the Aspen Physical Property System

See *Physical Property Models* for more information on the models listed below.

Pure Component Constants

Parameter	**Description**	**Model**
MW	Molecular weight	
TB	Normal boiling point	
TC	Critical temperature	

Parameter	Description	Model
PC	Critical pressure	
VC	Critical volume	
ZC	Critical compressibility factor	
DHFORM	Ideal gas heat of formation at 298.15 K	
DGFORM	Ideal gas Gibbs free energy of formation at 298.15 K	
OMEGA	Pitzer acentric factor	
DHVLB	Heat of vaporization at TB	

Pure Component Constants

Parameter	Description	Model
VB	Liquid molar volume at TB	
VLSTD	Standard liquid volume	
RGYR	Radius of gyration	
DELTA	Solubility parameter at 298.15 K	
GMUQR	UNIQUAC R parameter	UNIQUAC
GMUQQ	UNIQUAC Q parameter	UNIQUAC
PARC	Parachor †	
DHSFRM	Solid enthalpy of formation at 98.15 K	
DGSFRM	Solid Gibbs energy of formation at 298.15 K	
DHAQHG	Aqueous infinite dilution enthalpy of formation	Helgeson
DGAQHG	Aqueous infinite dilution Gibbs energy of formation	Helgeson
S25HG	Absolute entropy of aqueous species at 298.15 K	Helgeson

†Parachor is needed in estimating surface tension and radius of gyration.

Temperature-Dependent Property Correlation Parameters

Parameter	Description	Model
CPIG	Ideal gas heat capacity	General Pure Component Ideal Gas Heat Capacity

Parameter	Description	Model
CPLDIP	Liquid heat capacity	General Pure Component Liquid Heat Capacity
CPSPO1	Solid heat capacity	General Pure Component Solid Heat Capacity
PLXANT	Vapor pressure	General Pure Component Liquid Vapor Pressure
DHVLWT	Heat of vaporization	General Pure Component Heat of Vaporization
RKTZRA	Liquid molar volume	General Pure Component Liquid Molar Volume
OMEGHG	Helgeson OMEGA heat capacity (Born) coefficient	Helgeson
CHGPAR	Helgeson C Heat Capacity Coefficient	Helgeson
MUVDIP	Vapor viscosity	General Pure Component Vapor Viscosity
MULAND	Liquid viscosity	General Pure Component Liquid Viscosity
KVDIP	Vapor thermal conductivity	General Pure Component Vapor Thermal Conductivity
KLDIP	Liquid thermal conductivity	General Pure Component Liquid Thermal Conductivity
SIGDIP	Surface tension	General Pure Component Liquid Surface Tension

Binary Parameters

Parameter	Description	Model
WILSON/1, WILSON/2	Wilson parameters	Wilson
NRTL/1, NRTL/2	NRTL parameters	NRTL
UNIQ/1, UNIQ/2	UNIQUAC parameters	UNIQUAC
SRKKIJ	SRK parameter	SRK

UNIFAC Group Parameters

Parameter	Description	Model
GMUFR	UNIFAC R parameter	UNIFAC
GMUFQ	UNIFAC Q parameter	UNIFAC
GMUFDR	R parameter for Dortmund UNIFAC	Dortmund UNIFAC
GMUFDQ	Q parameter for Dortmund UNIFAC	Dortmund UNIFAC
GMUFLR	R parameter for Lyngby UNIFAC	Lyngby UNIFAC
GMUFLQ	Q parameter for Lyngby UNIFAC	Lyngby UNIFAC

Molecular Weight (MW)

If you use the general method to enter molecular structure on the **Components | Molecular Structure | General** sheet, the Aspen Physical Property System estimates molecular weight from the molecular formula. If you do not use the general method, then either:

- You must enter molecular weight using the **Methods | Parameters | Pure Component | Scalar** form
- The molecular weight must be available from the Aspen Physical Property System databank.

Normal Boiling Point (TB)

The Aspen Physical Property System uses the normal boiling point to estimate many other parameters, such as critical temperature and critical pressure, if they are missing. Normal boiling point is one of the most important pieces of information required for property/parameter estimation. Therefore, if you have an experimental normal boiling point, you should enter it using the **Methods | Parameters | Pure Component | Scalar** form.

PCES provides the following methods for estimating normal boiling point:

Method	Information Required
Joback	Structure
Ogata-Tsuchida	Structure
Gani	Structure
Mani	PC, Vapor pressure data (also uses TC if available)

Joback Method

The Joback method gives only an approximate estimate of normal boiling point. Absolute average error is 12.9 K for 408 diverse organic compounds. The Joback method is less accurate than the Ogata-Tsuchida method, but it is easier to use and applies to a wider range of compounds.

Table 3.5 in Physical Property Data lists the functional groups for the Joback method.

Ogata-Tsuchida Method

The Ogata-Tsuchida method is for compounds with a single functional group (such as -OH) and a radical type (such as methyl). This method performed reliably for 600 compounds tested; 80% were within 2 K, 89% were within 3 K, and 98% were within 5 K. Deviations larger than 5 K were generally for compounds containing the methyl radical.

Table 3.8 in Physical Property Data lists the functional groups for the Ogata-Tsuchida method.

Gani Method

The Gani method uses contributions from both first-order and second-order groups. The second order groups account for the effect of neighboring atoms. Use of second order groups results in higher accuracy. The estimation error of this method is about 2/5 of that of the Joback method. (*AIChE J*. 40,1697,1994).

Table 3.4A in Physical Property Data lists the functional groups for this method.

Mani Method

The Mani method was developed by Juan-Carlos Mani of Aspen Technology. This method estimates TB from the Riedel vapor pressure equation when one or two experimental temperature-vapor pressure data pairs are available. Such data is usually available for new specialty chemicals, especially for large molecules. This method can also be used to estimate TC and vapor pressure.

This method provides very accurate and reliable estimates of TB, TC and vapor pressure curve when some experimental vapor pressure data is available. It is very useful for complex compounds that decompose at temperatures below the normal boiling points.

The Riedel equation gives vapor pressure as a function of TB, TC and PC of the component. If one T-P pair is available, and TC and PC are known or estimated, the equation can be used to provide estimates of TB and vapor pressure. When two T-P pairs are available and PC is known or estimated, the equation can provide estimates of TB, TC, and vapor pressure.

Critical Temperature (TC)

PCES provides the following methods for estimating critical temperature :

Method	Information Required
Joback	Structure, TB
Lydersen	Structure, TB
Ambrose	Structure, TB
Fedors	Structure
Simple	MW, TB
Gani	Structure
Mani	PC, Vapor pressure

Joback Method

The Joback method is based on the Lydersen method, except it uses a larger database and has fewer functional groups. Joback tested approximately 400 organic compounds. The average relative error is 0.8%. The average error is 4.8K.

Table 3.5 in Physical Property Data lists the functional groups for the Joback method.

Lydersen Method

The Lydersen method is one of the first successful methods for estimating critical parameters. The functional groups listed in Table 3.7, Physical Property Data, are almost identical to those for the Joback method. The estimated error for TC is usually less than 2%. For high molecular weight nonpolar compounds (MW >> 100), the errors are 5% or higher.

Ambrose Method

The Ambrose method yields smaller errors than the Joback and Lydersen methods, but is more difficult to use. Table 3.1 in Physical Property Data lists the functional groups for this method. The errors for approximately 400 organic compounds are: average relative error = 0.7%; average error=4.3K.

Fedors Method

The Fedors method is not as accurate as the Joback, Lydersen, and Ambrose methods. For some compounds, the errors can be very large. Klincewicz and Reid (AIChE J. 30, 137, 1984) reported an average error of 4% for 199 compounds. Use this method only when TB is unknown. Table 3.4 in Physical Property Data lists the functional groups for this method.

Simple Method

The Simple method does not depend on molecular structure, but requires MW and TB as input. This method was developed by Klincewicz and Reid. The average error for about 200 diverse organic compounds tested is 2.3%.

Gani Method

The Gani method uses contributions from both first-order and second-order groups. The second order groups account for the effect of neighboring atoms. Use of second order groups results in higher accuracy (*AIChE J*. 40,1697,1994). Estimation accuracy is generally superior to other methods For 400 compounds tested, the average relative error is 0.85%. The average error is 4.85K. Table 3.4A in Physical Property Data lists the functional groups for this method.

Mani Method

The Mani method was developed by Juan-Carlos Mani of Aspen Technology. This method estimates TC from the Riedel equation when two experimental temperature-vapor pressure data pairs are available. Such data is usually available for new specialty chemicals, especially for large molecules. This method can also be used to estimate TB and vapor pressure.

This method provides very accurate and reliable estimate of TB, TC and vapor pressure curve when some experimental vapor pressure data is available. It is very useful for complex compounds that decompose at temperatures below the normal boiling points.

The Riedel equation gives vapor pressure as a function of TB, TC and PC of the component. If one T-P pair is available, and TC and PC are known or estimated, the equation can be used to provide estimates of TB and vapor pressure. When two T-P pairs are available and PC is known or estimated, the equation can provide estimates of TB, TC, and vapor pressure.

Critical Pressure (PC)

PCES provides the following methods for estimating critical pressure:

Method	Information Required
Joback	Structure
Lydersen	Structure, MW
Ambrose	Structure, MW
Gani	Structure

Joback Method

The Joback method is based on the Lydersen method, except it uses a larger database and has fewer functional groups. For 390 organic compounds tested, the average relative error is 5.2%; the average error is 2.1bar.

Table 3.5 in Physical Property Data lists the functional groups for the Joback method.

Lydersen Method

The Lydersen method is one of the first successful methods for estimating critical parameters. The functional groups listed in Table 3.7, Physical Property Data, are almost identical to those for the Joback method. The estimated error is approximately 4%.

Ambrose Method

The Ambrose method yields smaller errors than the Joback and Lydersen methods, but is more difficult to use. Table 3.1 in Physical Property Data lists the functional groups for this method. For 390 organic compounds tested, the average relative error is 4.6 %; the average error is 1.8 bar.

Gani Method

The Gani method uses contributions from both first-order and second-order groups. The second order groups account for the effect of neighboring atoms. Use of second order groups results in higher accuracy (*AIChE J*. 40,1697,1994). Estimation accuracy is generally superior to other methods. For 390 organic compounds tested, the average relative error is 2.89 %; the average error is 1.13 bar. Table 3.4A in Physical Property Data lists the functional groups for this method.

Critical Volume (VC)

PCES provides the following methods for estimating critical volume:

Method	Information Required
Joback	Structure
Lydersen	Structure
Ambrose	Structure
Riedel	TB, TC, PC
Fedors	Structure
Gani	Structure

Joback Method

The Joback method is based on the Lydersen method, except it uses a larger database and has fewer functional groups. For 310 organic compounds tested, the average relative error is 2.3%; the average error is 7.5 cc/mole.

Table 3.5 in Physical Property Data lists the functional groups for the Joback method.

Lydersen Method

The Lydersen method is one of the first successful methods for estimating critical parameters. The functional groups listed in Table 3.7, Physical Property Data are almost identical to those for the Joback method. The estimated error is approximately 4%.

Ambrose Method

The Ambrose method yields smaller errors than the Joback and Lydersen methods, but is more difficult to use. Table 3.1 in Physical Property Data lists the functional groups for this method. For 310 organic compounds tested, the average relative error is 2.8%; the average error is 8.5 cc/mole.

Riedel Method

This method is recommended for hydrocarbons only.

Fedors Method

The Fedors method is not as accurate as the Joback, Lydersen, and Ambrose methods. For some compounds, the errors can be very large. Klincewicz and Reid (AIChE J. 30, 137, 1984) reported an average error of 4% for 199 compounds. Use this method only when TB is unknown. Table 3.4 in Physical Property Data lists the functional groups for this method.

Gani Method

The Gani method uses contributions from both first-order and second-order groups. The second order groups account for the effect of neighboring atoms. Use of second order groups results in higher accuracy (*AIChE J*. 40,1697,1994). Estimation accuracy is generally superior to other methods. For 310 organic compounds tested, the average relative error is 1.79%; the average error is 6.0 cc/mole. Table 3.4A in Physical Property Data lists the functional groups for this method.

Critical Compressibility Factor (ZC)

The Aspen Physical Property System calculates the critical compressibility factor (ZC) by:

$$Z_c = \frac{P_c V_c}{R T_c}$$

Where:

R = Universal gas constant
P_c = Critical pressure
V_c = Critical volume
T_c = Critical temperature

Ideal Gas Heat of Formation (DHFORM)

PCES provides the following methods for estimating the ideal gas heat of formation at 298.15 K:

Method	Information Required
Benson	Structure
Joback	Structure
BensonR8	Structure
Gani	Structure

All methods are group contribution methods that apply to a wide range of compounds. The Benson Method is recommended.

The heat of formation of the ideal gas is calculated relative to the zero enthalpy of the constituent elements at 25°C and 1 atm in their natural phases (for instance, solid graphite for carbon, liquid for mercury, and H_2 gas for hydrogen).

Benson Method

The Benson method is a second-order group contribution method. This method:

- Accounts for the effect of neighboring atoms
- Is more complex to use than the Joback method
- Reports more accurate results than Joback (average error is 3.7 kJ/mol)

Table 3.2 in Physical Property Data lists the functional groups for the Benson method.

Joback Method

The Joback method is a first-order group contribution method. It is simpler to use than the other available methods, but is less accurate. Reported average error is 8.9 kJ/mol.

Table 3.5 in Physical Property Data lists the functional groups for the Joback method.

BensonR8 Method

This is the Benson method provided with Release 8 of Aspen Plus. It is retained for upward compatibility. The Benson method is preferred.

Gani Method

The Gani method uses contributions from both first-order and second-order groups. The second order groups account for the effect of neighboring atoms. Use of second order groups results in higher accuracy than the Joback method (average error is 3.71 kJ/mol) (*AIChE J*. 40,1697,1994).

Table 3.4A in Physical Property Data lists the functional groups for this method.

Ideal Gas Gibbs Free Energy of Formation (DGFORM)

PCES provides the following methods for estimating ideal gas Gibbs free energy of formation at 298.15 K:

Method	Information Required
Joback	Structure
Benson	Structure
Gani	Structure

The Gibbs energy of formation of the ideal gas is calculated relative to the zero Gibbs energy of the constituent elements at 25°C and 1 atm in their natural phases (for instance, solid graphite for carbon, liquid for mercury, and H_2 gas for hydrogen).

Benson Method

The Benson method is a second-order group contribution method. For this property, the Benson method requires you to enter the symmetry number and the number of possible optical isomers, if applicable. The Aspen Physical Property System does not generate this information automatically from the general molecular structure.

Table 3.2 in Physical Property Data lists the functional groups for the Benson method.

Joback Method

The Joback method is a first-order group contribution method. It is simpler to use than the other available methods, but is less accurate. Reported errors are in the range of 5 to 10 kJ/mol. The errors are larger for complex materials.

Table 3.5 in Physical Property Data lists the functional groups for the Joback method.

Gani Method

The Gani method uses contributions from both first-order and second-order groups. The second order groups account for the effect of neighboring atoms. Use of second order groups results in higher accuracy (*AIChE J*. 40,1697,1994).

The Gani method:

- Is more complex to use than the Joback method
- Reports more accurate results than Joback (average error is 3.24 kJ/-mol)

Table 3.4A in Physical Property Data lists the functional groups for this method

Acentric Factor (OMEGA)

PCES provides two methods for estimating acentric factor:

- Definition method
- Lee-Kesler method

Definition Method

When you use the definition method, the acentric factor is calculated from its definition:

$$\omega_i = -\log_{10}\left(\frac{P_i^*}{P_{ci}}\right) - 1.0$$

Where P_i^* is vapor pressure calculated at reduced temperature, (T/T_c) of 0.7.

When you use the definition method, the vapor pressure correlation parameters PLXANT, TC, and PC must be available from the databank or estimated.

Lee-Kesler Method

The Lee-Kesler method depends on TB, TC, and PC. This method is recommended for hydrocarbons. Lee and Kesler reported that this method yields values of acentric factors close to those selected by Passut and Danner (*Ind. Eng. Chem. Process Des. Dev.*12, 365, 1973).

Heat of Vaporization at TB (DHVLB)

PCES estimates heat of vaporization at the normal boiling point by applying the Watson equation (DHVLWT) from the General Pure Component Heat of Vaporization correlation at TB.

Liquid Molar Volume at TB (VB)

PCES estimates liquid molar volume at the normal boiling point by applying the Rackett equation (RKTZRA) from the General Pure Component Liquid Molar Volume model at TB.

You can also opt to specify this value. To do so:

1. On the **Set Up** tab of the **Fluid Package** view, click **Edit Properties**.
2. On the **Editing Properties for...** view, select the **VB** property in the left-hand pane.
3. Edit the **Property Value**.

Standard Liquid Volume (VLSTD)

PCES estimates standard liquid volume by applying the Rackett equation (RKTZRA) from the General Pure Component Liquid Molar Volume correlation at 60° F.

Radius of Gyration (RGYR)

PCES estimates radius of gyration from parachor (PARC).

Solubility Parameter (DELTA)

The solubility parameter is calculated from the definition.

UNIQUAC R and Q Parameters (GMUQR, GMUQQ)

PCES provides the Bondi method for estimating the UNIQUAC R and Q parameters. This method requires only molecular structure as input. Table 3.3 in Physical Property Data in the help lists the functional groups.

Parachor (PARC)

PCES provides one method for estimating Parachor. The Parachor method is a group-contribution method. The functional groups for this method are listed in Table 3.10 in Physical Property Data.

Parachor is not used in any built-in models, but it may be used by user models. It is also used to estimate radius of gyration.

Solid Standard Enthalpy of Formation (DHSFRM)

Only the Mostafa method is available for estimating solid standard enthalpy of formation.

The heat of formation of the solid is calculated relative to the zero enthalpy of the constituent elements at 25°C and 1 atm in their natural phases (for instance, solid graphite for carbon, liquid for mercury, and H_2 gas for hydrogen).

Mostafa Method

The Mostafa method is a group contribution method. This method applies to solid inorganic salts which can be divided to cations, anions and ligands. Reported average errors for 938 diverse solid inorganic salts was 2.57% (*Ind. Eng. Chem. RES.*, 34, 4577, 1995).

Table 3.7A in Physical Property Data lists the functional groups for this method.

Solid Standard Gibbs Free Energy of Formation (DGSFRM)

Only the Mostafa method is available for estimating solid standard Gibbs free energy of formation.

The Gibbs energy of formation of the solid is calculated relative to the zero Gibbs energy of the constituent elements at 25°C and 1 atm in their natural phases (for instance, solid graphite for carbon, liquid for mercury, and H_2 gas for hydrogen).

Mostafa Method

The Mostafa method is a group contribution method. This method applies to solid inorganic salts which can be divided to cations, anions and ligands. Reported average errors for 687 diverse solid inorganic salts was 2.06% (*Ind. Eng. Chem. RES.*, 34, 4577, 1995).

Table 3.7A in Physical Property Data lists the functional groups for this method.

Standard Enthalpy of Formation of Aqueous Species (DHAQHG)

PCES provides the following methods for estimating standard enthalpy of formation of aqueous species for the Helgeson electrolyte model:

Method	Information Required
AQU-DATA	DHAQFM
THERMO	DGAQFM, S025C
AQU-EST1	DGAQFM
AQU-EST2	S025C

The heat of formation of the aqueous components is calculated relative to the zero enthalpy of the constituent elements at 25°C and 1 atm in their natural phases (for instance, solid graphite for carbon, liquid for mercury, and H_2 gas for hydrogen).

AQU-DATA Method

The AQU-DATA method uses directly experimental standard enthalpy of formation at infinite dilution (DHAQFM) if it exists in the databank.

THERMO Method

The THERMO method estimates standard enthalpy of formation according to thermodynamic relationship if DGAQFM and S025C exist in the databank, as follows:

$$DHAQHG = DGAQFM + 298.15 \times (\mathrm{S025C} - \mathrm{S025E})$$

where S025E is the sum of absolute entropy of the constituent elements of a compound at 25°C.

AQU-EST1 Method

If DGAQFM is in the databank, the AQU-EST1 method estimates standard enthalpy of formation using an empirical relation developed by Aspen Technology, as follows:

$$DHAQHG = 1.105 \times DGAQFM - 12822.8$$

AQU-EST2 Method

If S025C is in the databank, the AQU-EST2 method estimates standard enthalpy of formation using an empirical relation developed by Aspen Technology, as follows:

$$DHAQHG = 122111.3214 + 3137.4034 \times (\mathrm{S025C} - \mathrm{S025E})$$

where S025E is the sum of absolute entropy of the constituent elements of a compound at 25°C.

Standard Gibbs Free Energy of Formation of Aqueous Species (DGAQHG)

PCES provides the following methods for estimating standard Gibbs free energy of formation of aqueous species for the Helgeson electrolyte model:

Method	Information Required
AQU-DATA	DGAQFM
THERMO	DHAQFM, S025C

Method	Information Required
AQU-EST1	DHAQFM
AQU-EST2	S025C

The Gibbs energy of formation of the aqueous components is calculated relative to the zero Gibbs energy of the constituent elements at 25°C and 1 atm in their natural phases (for instance, solid graphite for carbon, liquid for mercury, and H_2 gas for hydrogen).

AQU-DATA Method

The AQU-DATA method uses directly experimental standard Gibbs free energy of formation at infinite dilution (DGAQFM) if it exists in the databank.

THERMO Method

If DHAQFM and S025C are in the databank, the THERMO method estimates standard Gibbs free energy of formation according to thermodynamic relationship, as follows:

$$DGAQHG = DHAQFM - 298.15 \times (\mathrm{S025C} - \mathrm{S025E})$$

where S025E is the sum of absolute entropy of the constituent elements of a compound at 25°C.

AQU-EST1 Method

If DHAQFM is in the databank, the AQU-EST1 method estimates standard Gibbs free energy of formation using an empirical relation developed by Aspen Technology, as follows:

$$DGAQHG = \frac{(DHAQFM + 12822.8)}{1.105}$$

AQU-EST2 Method

If S025C is in the databank, the AQU-EST2 method estimates standard Gibbs free energy of formation using an empirical relation developed by Aspen Technology, as follows:

$$DGAQHG = 122110.2752 + 2839.2534 \times (S025C - S025E)$$

where S025E is the sum of absolute entropy of the constituent elements of a compound at 25°C.

Absolute Entropy of Aqueous Species (S25HG)

PCES provides the following methods for estimating absolute entropy of aqueous species for the Helgeson electrolyte model:

Method	Information Required
AQU-DATA	S025C
THERMO	DGAQFM, DHAQFM
AQU-EST1	DGAQFM
AQU-EST2	DHAQFM

AQU-DATA Method

The AQU-DATA method uses directly the experimental absolute entropy (S025C) if it exists in the databank.

THERMO Method

If DGAQFM and DHAQFM are in the databank, the THERMO method estimates absolute entropy according to thermodynamic relationship, as follows:

$$\mathrm{S25HG} = \frac{(DHAQFM - DGAQFM)}{298.15} + \mathrm{S025E}$$

where S025E is the sum of absolute entropy of the constituent elements of a compound at 25°C.

AQU-EST1 Method

If DGAQFM is in the databank, the AQU-EST1 method estimates absolute entropy using an empirical relation developed by Aspen Technology, as follows:

$$\mathrm{S25HG} = 3.52205 \times 10^{-4} \times DGAQFM - 43.00788 + \mathrm{S025E}$$

where S025E is the sum of absolute entropy of the constituent elements of a compound at 25°C.

AQU-EST2 Method

If DHAQFM is in the databank, the AQU-EST2 method estimates absolute entropy using an empirical relation developed by Aspen Technology, as follows:

$$\mathrm{S25HG} = 3.187349x10^{-4} \times DHAQFM - 38.9208 + \mathrm{S025E}$$

Ideal Gas Heat Capacity (CPIG)

PCES provides three methods for estimating ideal gas heat capacity:

Method	Information Required
Data	Ideal gas heat capacity data
Benson	Structure
Joback	Structure

PCES uses the Aspen equation from the General Pure Component Ideal Gas Heat Capacity model for this property. Both the Benson and Joback methods are group-contribution methods that apply to a wide range of compounds.

Do not use the Benson or Joback methods outside the temperature range of 280 to 1100 K. Errors are generally less than 1 to 2%.

Benson Method

Benson is the recommended method. It accounts for the effect of neighboring atoms. In comparison with the Joback method, Benson:

- Is more complex to use
- Reports more accurate results (average error 1.1% for 27 diverse compounds)

Table 3.2 in Physical Property Data lists the functional groups for the Benson method.

Joback Method

The Joback method is a first-order group contribution method. It is simpler to use than the Benson method, but is less accurate. Reported average error is 1.4% for 28 diverse components.

Table 3.5 in Physical Property Data lists the functional groups for the Joback method.

Data Method

The Data method determines parameters for the ideal gas heat capacity polynomial. Experimental ideal gas heat capacity data are fitted. You enter this data on the **Data | Pure Component** form.

Liquid Heat Capacity (CPL, from CPLDIP)

PCES provides the following methods for estimating liquid heat capacity:

Method	Information Required
Data	Liquid heat capacity data
Ruzicka	Structure

The DIPPR equation (parameter CPLDIP) from the General Pure Component Liquid Heat Capacity correlation is used for this property.

Data Method

The Data method determines the DIPPR liquid heat capacity correlation parameters by fitting experimental liquid heat capacity data. Enter this data on the **Data | Pure Component** form.

Ruzicka Method

The Ruzicka method is a group contribution method for estimating parameters for the DIPPR liquid heat capacity correlation. The parameters are valid from the melting point to the normal boiling point. This method requires only molecular structure as input. For 9772 diverse compounds, reported average errors were 1.9% and 2.9% for nonpolar and polar compounds, respectively (*J. Phys. Chem. Ref. Data*, 22, 597, 1993; 22, 619, 1993).

Table 3.11A in Physical Property Data lists the functional groups for this method.

Solid Heat Capacity (CPS, from CPSPO1)

PCES provides the following methods for estimating solid heat capacity:

Method	Information Required
Data	Solid heat capacity data
Mostafa	Structure

The Aspen equation (parameter CPSPO1) from the General Pure Component Solid Heat Capacity correlation is used for this property.

Data Method

The Data method determines the solid heat capacity correlation parameters by fitting experimental liquid heat capacity data. You enter this data on the **Data | Pure Component** form.

Mostafa Method

The Mostafa method is a group contribution method for estimating parameters for the solid heat capacity correlation. This method is applied to solid inorganic salts which are divided to cations, anions and ligands. Reported average errors for 664 diverse solid inorganic salts, was 3.18% (*Ind. Eng. Chem. Res.*, 35, 343, 1996).

Table 3.7A in Physical Property Data lists the functional groups for this method.

Vapor Pressure (PL, from PLXANT)

PCES provides the following methods for estimating vapor pressure:

Method	Information Required
Data	Vapor pressure data
Riedel	TB, TC, PC, (vapor pressure data)
Li-Ma	Structure, TB, (vapor pressure data)
Mani	PC, (vapor pressure data) (also uses TC if available)

The Extended Antoine equation (parameter PLXANT) from the General Pure Component Liquid Vapor Pressure model is used for this property.

Data Method

The Data method determines parameters for the Extended Antoine equation by fitting experimental vapor pressure data that you enter on the **Data | Pure Component** form.

Riedel Method

The Riedel method estimates parameters for the Extended Antoine vapor pressure equation by applying the Riedel parameter and the Plank-Riedel constraint at the critical point. It also makes use of the condition that at the normal boiling point, the vapor pressure is 1 atm. The parameters are valid from TB to TC. This method is accurate for nonpolar compounds, but not for polar compounds.

Li-Ma Method

The Li-Ma method is a group contribution method for estimating parameters for the Extended Antoine vapor pressure equation. The parameters are valid from TB to TC. This method is accurate for polar and nonpolar compounds. For 28 diverse compounds, the reported average error was 0.61% (*Fluid Phase Equilibria*, 101, 101, 1994).

Table 3.6A in Physical Property Data lists the functional groups for this method.

Mani Method

The Mani method was developed by Juan-Carlos Mani of Aspen Technology. This method estimates parameters for the Extended Antoine vapor pressure equation using the Riedel equation when one or two experimental temperature-vapor pressure data pairs are available. Such data is usually available for new specialty chemicals, especially for large molecules. This method can also be used to estimate TB and TC.

This method provides very accurate and reliable estimates of TB, TC and vapor pressure curve when some experimental vapor pressure data values are available. It is very useful for complex compounds that decompose at temperatures below the normal boiling points. The vapor pressure equation is applicable from the lowest temperature data point to the critical temperature.

The Riedel equation gives vapor pressure as a function of TB, TC and PC of the component. If one T-P pair is available, and TC and PC are known or estimated, the equation can be used to provide estimates of TB and vapor pressure. When two T-P pairs are available and PC is known or estimated, the equation can provide estimates of TB, TC, and vapor pressure.

Heat of Vaporization (DHVL, from DHVLWT)

PCES provides the following methods for estimating heat of vaporization:

Method	Information Required
Data	Heat of vaporization data
Definition	TC, PC, PL, (Heat of vaporization data)
Vetere	MW, TB, (Heat of vaporization data)
Gani	Structure, (Heat of vaporization data)
Ducros	Structure, (Heat of vaporization data)
Li-Ma	Structure, TB, (Heat of vaporization data)

The Watson equation (parameter DHVLWT) from the General Pure Component Heat of Vaporization model is used for this property.

Data Method

The Data method determines the Watson parameters by fitting experimental heat of vaporization data that you enter on the **Data | Pure Component** form.

Definition Method

The Definition method calculates heat of vaporization from the Clausius-Clapeyron equation. It requires vapor pressure, TC, and PC as input. The calculated heat of vaporization values are used to determine the parameters for the Watson equation. When the Riedel method was used to estimate vapor pressure, reported average error for the heat of vaporization was 1.8% for 94 compounds.

Vetere Method

The Vetere method estimates heat of vaporization at TB, then uses the Watson equation to extrapolate heat of vaporization to TC. Reported average error is 1.6%.

Gani Method

The Gani method is a group contribution method for estimating heat of vaporization at 298K. It uses the Watson equation to extrapolate heat of vaporization to TC. This method requires only molecular structure as input.

Table 3.4A in Physical Property Data lists the functional groups for this method.

Ducros Method

The Ducros method is a group contribution method for estimating heat of vaporization at 298K. It uses the Watson equation to extrapolate heat of vaporization to TC (*Thermochimica Acta*, 36, 39, 1980; 44, 131, 1981; 54, 153, 1982; 75, 329, 1984). This method:

- Uses more complex structure correction
- Can be applied to organo-metallic compounds

Table 3.3A in Physical Property Data lists the functional groups for this method.

Li-Ma Method

The Li-Ma method is a group contribution method for estimating heat of vaporization at different temperatures. This method requires molecular structure and TB as input. Reported average error for 400 diverse compounds was 1.05% (*Fluid Phase Equilibria*, 1997).

Table 3.6A in Physical Property Data lists the functional groups for this method.

Liquid Molar Volume (VL, from RKTZRA)

PCES provides three methods for estimating liquid molar volume:

Method	Information Required
Data	Liquid molar volume data
Gunn-Yamada	TC, PC.OMEGA
Le Bas	Structure

The Rackett equation (parameter RKTZRA) from the General Pure Component Liquid Molar Volume model is used for this property.

Gunn-Yamada Method

The Gunn-Yamada method estimates saturated liquid molar volume, when the reduced temperature is less than 0.99. The calculated values are used to determine the Rackett parameter. This method:

- Applies to nonpolar and slightly polar compounds
- Is more accurate than the Le Bas method

Le Bas Method

The Le Bas method estimates liquid molar volume at TB. The result is used to determine the Rackett parameter. For 29 diverse compounds, an average error of 3.9% is reported. This method requires only molecular structure as input. Table 3.6 in Physical Property Data lists the functional groups.

Data Method

The Data method determines the Rackett parameter by fitting the experimental liquid molar volume data that you enter on the **Data | Pure Component** form.

Born Coefficient (OMEGHG)

Only the Helgeson method is available for estimating the Born coefficient of aqueous species for the Helgeson electrolyte model. This method requires S25HG and CHARGE as input.

Helgeson Capacity Parameters (CHGPAR)

PCES provides the following methods for estimating the Helgeson capacity parameters of aqueous species for the Helgeson electrolyte model:

Method	Information Required
HG-AUQ	OMEGHG, CPAQ0
HG-CRIS	OMEGHG, S25HG, CHARGE, IONTYP
HG-EST	OMEGHG, S25HG

HG-AQU Method

The HG-AQU method estimates the Helgeson capacity parameters from the infinite dilution heat capacity CPAQ0.

HG-CRIS Method

The HG-CRIS method estimates the Helgeson capacity parameters according to the Criss-Cobble method.

HG-EST Method

The HG-EST method estimates the Helgeson capacity parameters using an empirical relation developed by Aspen Technology.

Vapor Viscosity (MUV, from MUVDIP)

PCES provides the following methods for estimating vapor viscosity:

Method	Information Required
Data	Vapor viscosity data
Reichenberg	Structure, MW,TC, PC

The DIPPR equation (parameter MUVDIP) from the General Pure Component Vapor Viscosity correlation is used for this property.

Reichenberg Method

Reichenberg is a group-contribution method. For nonpolar compounds, the expected error is between 1 and 3%. For polar compounds, the errors are higher, but usually less than 4%. Table 3.11 in Physical Property Data lists the functional groups for this method.

Data Method

The Data method determines the General Pure Component Vapor Viscosity correlation parameters by fitting experimental vapor viscosity data you enter on the **Data | Pure Component** form.

Liquid Viscosity (MUL, from MULAND)

PCES provides the following methods for estimating liquid viscosity:

Method	Information Required
Data	Liquid viscosity data
Orrick-Erbar	Structure, MW, VL, ZC, TC, PC
Letsou-Stiel	MW, TC, PC, OMEGA

The Andrade equation (parameter MULAND) from the General Pure Component Liquid Viscosity model is used for this property.

Orrick-Erbar Method

Orrick-Erbar is a group-contribution method that depends on liquid molar volume. It is limited to low temperatures, ranging from above the freezing point to the reduced temperature of 0.75. This method:

- Is not reliable for highly branched structures
- Does not apply to inorganic liquids or sulfur compounds
- Reports an average error of 15% for 188 organic liquids

Table 3.9 in Physical Property Data lists the functional groups for this method.

Letsou-Stiel Method

The Letsou-Stiel method is appropriate for high temperatures and for reduced temperatures of 0.76 to 0.92. The average error is 3% for 14 liquids.

Data Method

The Data method determines the Andrade parameters by fitting experimental liquid viscosity data that you enter on the **Data | Pure Component** form.

Vapor Thermal Conductivity (KV, from KVDIP)

No estimation method is available for estimating vapor thermal conductivity. You can use the Data method to fit experimental data directly to the DIPPR vapor thermal conductivity correlation (parameter KVDIP). Use the **Data | Pure Component** form to enter experimental vapor thermal conductivity data.

Liquid Thermal Conductivity (KL, from KLDIP)

PCES provides the following methods for estimating liquid thermal conductivity:

Method	Information Required
Data	Liquid thermal conductivity data
Sato-Riedel	MW, TB, TC

The DIPPR equation (parameter KLDIP) from the General Pure Component Liquid Thermal Conductivity correlation is used for this property.

Sato-Riedel Method

When you use the Sato-Riedel method, accuracy varies widely from 1 to 20% for the compounds tested. The accuracy is poor for light and branched hydrocarbons.

Data Method

The Data method determines the DIPPR liquid thermal conductivity correlation parameters. This method fits experimental liquid thermal conductivity data. Enter this data on the **Data | Pure Component** form.

Surface Tension (SIGMA, from SIGDIP)

PCES provides the following methods for estimating surface tension:

Method	Information Required
Data	Surface tension data

Method	Information Required
Brock-Bird	TB, TC, PC
Macleod-Sugden	TB, TC, PC, VL, PARC
Li-Ma	Structure, TB

The DIPPR equation (parameter SIGDIP) from the General Pure Component Liquid Surface Tension correlation is used for this property.

Data Method

The Data method determines the DIPPR surface tension correlation parameters by fitting experimental surface tension data. Enter this data on the **Data | Pure Component** form.

Brock-Bird Method

The Brock-Bird method applies to non-hydrogen-bonded liquids. The expected error is less than 5%.

Macleod-Sugden Method

The Macleod-Sugden method applies to nonpolar, polar, and hydrogen-bonded liquids. For hydrogen-bonded liquids, errors are normally less than 5 to 10%.

Li-Ma Method

The Li-Ma method is a group contribution method for estimating surface tension at different temperature. This method requires only molecular structure and TB as input. Reported average error for 427 diverse compounds was 1.09% (*Fluid Phase Equilibria*, 118, 13, 1996).

Table 3.6A in Physical Property Data lists the functional groups for this method.

Binary Parameters (WILSON, NRTL, UNIQ, SRKKIJ)

PCES estimates binary parameters for the WILSON, NRTL, UNIQUAC, and SRK models, using infinite-dilution activity coefficients. Infinite-dilution activity coefficients can be supplied by:

- Laboratory data entered on the **Data | Mixture** form, with data type=GAMINF
- Estimation, using the UNIFAC, UNIF-LL, UNIF-DMD or UNIF-LBY method

SRKKIJ can also be estimated using the ASPEN method from critical volume when only light gases and hydrocarbons are present in the system.

For best results, use experimental infinite-dilution activity coefficient data. Of the four UNIFAC methods, the Dortmund method (UNIF-DMD) gives the most accurate estimate of infinite-dilution activity coefficients. This method is recommended. See UNIFAC, UNIFAC (Dortmund modified), and UNIFAC (Lyngby modified) in *Physical Property Models* for detailed descriptions of these methods.

If the data is at a single temperature, PCES estimates only the second element of the parameter, such as WILSON/2. If the data cover a temperature range, PCES estimates both elements of the parameter, such as WILSON/1 and WILSON/2.

For NRTL, the alpha parameter (c_{ij}) is by default set to 0.3, but the value can be changed, and in some cases such change may be necessary. The procedure estimates NRTL coefficients from limiting activity coefficients, and does not necessarily represent the concentration range (such as non-zero molefractions) on which the alpha parameter has a marked influence, especially in two-liquid systems. You can set c_{ij} for the binary system to the appropriate value before running the estimation.

Value	Systems for which this value is recommended
0.30	Nonpolar substances, nonpolar with polar non-associated liquids, small deviations from ideality
0.20	Saturated hydrocarbons with polar non-associated liquids and systems that exhibit liquid-liquid immiscibility
0.47	Strongly self-associated substances with nonpolar substances

UNIFAC R and Q Parameters (UNIFACR, UNIFACQ, UNIFLR, UNIFLQ, UNIFDR, UNIFDQ)

PCES provides the Bondi method for estimating the R and Q parameters for UNIFAC functional groups. The Aspen Physical Property System uses these parameters in the UNIFAC, Dortmund UNIFAC, and Lyngby UNIFAC models. The Bondi method requires only molecular structure as input. Enter the molecular structure using the Bondi method on the **Components | Molecular Structure | Functional Group** sheet. Table 3.3 in Physical Property Data lists the functional groups for the Bondi method.

For property method	Estimate this property	To estimate this parameter
UNIFAC	UNIFACR	GMUFR
	UNIFACQ	GMUFQ
UNIFAC (Dortmund)	UNIFDR	GMUFDR
	UNIFDQ	GMUFDQ
UNIFAC (Lyngby)	UNIFLR	GMUFLR

For property method	Estimate this property	To estimate this parameter
	UNIFLQ	GMUFLQ

Description of Estimation Methods

This section describes the:

- Methods available for estimating property parameters
- Application range for each method (when appropriate)
- Expected error for each method (when appropriate)

The expected error information can help you to evaluate a method.

Methods

Ambrose

The Ambrose method can be used to estimate: TC, PC, and VC. To use this method, you must supply molecular structure and normal boiling point for estimating TC; molecular structure and molecular weight for estimating PC; and molecular structure for estimating VC. You can list the functional groups for the Ambrose method using the **Components | Molecular Structure | Functional Group** sheet.

The Ambrose method yields smaller errors than the Joback and Lydersen methods, but is more difficult to use. The errors for approximately 400 organic compounds are summarized below:

Parameter	No. of Compounds	Avg. Relative Error(%)	Avg. Error
TC	400	0.7	4.3 (K)
PC	390	4.6	1.8 (bar)
VC	310	2.8	8.5 (cc/mol)

Aqu-data

The Aqu-data method can estimate standard enthalpy of formation of aqueous species (DHAQHG), standard Gibbs free energy of formation of aqueous species (DGAQHG), and absolute entropy of aqueous species (S25HG) for the Helgeson electrolyte model. This method uses directly experimental data in the databank to estimate the parameters for the Helgeson electrolyte model.

This method uses	To estimate
standard enthalpy of formation at infinite dilution (DHAQFM)	standard enthalpy of formation of aqueous species (DHAQHG)

This method uses	To estimate
standard Gibbs free energy of formation at infinite dilution (DGAQFM)	standard Gibbs free energy of formation of aqueous species (DGAQHG)
absolute entropy (S025C)	absolute entropy of aqueous species (S25HG)

Aqu-est1

The Aqu-est1 method can estimate standard enthalpy of formation of aqueous species (DHAQHG), standard Gibbs free energy of formation of aqueous species (DGAQHG), and absolute entropy of aqueous species (S25HG) for the Helgeson electrolyte model.

This method uses an empirical relation developed by Aspen Technology, as follows:

- DHAQHG = 1.105 × DGAQFM – 12822.8
- DGAQHG = (DHAQFM + 12822.8) / 1.105
- S25HG = 3.52205×10^{-4} × DGAQFM – 43.00788 + S025E

where S025E is the sum of absolute entropy of the constituent elements of a compound at 25 °C

Aqu-est2

The AQU-EST2 method can estimate standard enthalpy of formation of aqueous species (DHAQHG), standard Gibbs free energy of formation of aqueous species (DGAQHG), and absolute entropy of aqueous species (S25HG) for the Helgeson electrolyte model.

This method uses empirical relation developed by Aspen Technology, as follows:

DHAQHG = 122111.3214 + 3137.4034 × (S025C – S025E)

DGAQHG = 122110.2752 + 2839.2534 × (S025C – S025E)

S25HG = 3.187349×10^{-4} × DHAQFM – 38.9208 + S025E

where S025E is the sum of absolute entropy of the constituent elements of a compound at 25 °C.

Benson

The Benson method can be used to estimate ideal gas heat of formation, DHFORM, ideal gas Gibbs free energy of formation, DGFORM, and ideal gas heat capacity, CPIG. To use this method, you must supply molecular structure. You can list the functional groups for the Benson method using the **Components | Molecular Structure | Functional Group** sheet.

The Benson method is more complex to use than other methods because it accounts for the effect of the neighboring atoms. However, it is much more accurate and is recommended over the Joback method. The Benson method is applicable to a wide range of compounds.

For DHFORM, the reported average error is 3.7 kJ/mol.

For CPIG, the reported average error is 1.1% for 27 diverse components. It should not be used outside the temperature range of 280 to 1100 K.

For DGFORM, the Benson method requires you to enter the symmetry number and the number of possible optical isomers, if applicable. The Aspen Physical Property System does not generate this information automatically from the general molecular structure.

BensonR8

The BensonR8 method can be used to estimate standard enthalpy of formation, DHFORM, and ideal gas heat capacity, CPIG. This is the Benson method provided with Release 8 of Aspen Plus. It is retained for upward compatibility. The Benson method is preferred.

Bondi

The Bondi method can be used to estimate the UNIQUAC R and Q parameters for molecular components and the UNIFAC R and Q parameters for groups. To use this method, you must supply molecular structure. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

Brock-Bird

The Brock-Bird method can be used to estimate surface tension. To use this method, you must supply normal boiling point, critical temperature, and critical pressure. The Brock-Bird method is applicable to non-hydrogen-bonded liquids. The expected error is less that 5%.

Data

The Data method determines parameters by fitting experimental data you supply using the **Data** forms. This method is similar to using the Aspen Physical Property System Data Regression System (DRS), but is easier.

The table below lists the parameters determined for the following properties:

Property	Parameter Determined
Ideal gas heat capacity	CPIG
Liquid heat capacity	CPLDIP
Solid heat capacity	CPSPO1
Vapor pressure	PLXANT

Property	Parameter Determined
Heat of vaporization	DHVLWT
Liquid molar volume	RKTZRA
Liquid viscosity	MULAND
Vapor viscosity	MUVDIP
Liquid thermal conductivity	KLDIP
Vapor thermal conductivity	KVDIP
Surface tension	SIGDIP
Wilson binary parameters	WILSON/1, WILSON/2
NRTL binary parameters	NRTL/1, NRTL/2
UNIQUAC binary parameters	UNIQ/1, UNIQ/2

Definition

The Definition method calculates the property from its basic definitions.

For critical compressibility factor, ZC, the definition requires TC, PC, and VC.

For acentric factor, OMEGA, the definition requires vapor pressure. Therefore, the vapor pressure correlation parameters, PLXANT, must be available as well as TC and PC.

For solubility parameter, DELTA, the definition requires TB, TC, PC, DHVL, and VL.

For heat of vaporization, the parameters DHVLWT are calculated from the Clausius-Clapeyron equation. This method requires vapor pressure, TC, and PC as input. For 94 compounds, an average error of 1.8% has been reported for the heat of vaporization at TB when the Riedel method was used to estimate vapor pressure.

Ducros

The Ducros method is a group contribution method for estimating heat of vaporization at 298K. It uses the Watson equation to extrapolate heat of vaporization to TC (*Thermochimica Acta*, 36, 39, 1980; 44, 131, 1981; 54, 153, 1982; 75, 329, 1984). This method:

- Uses more complex structure correction
- Can be applied to organo-metallic compounds

Fedors

The Fedors method can be used to estimate TC and VC. To use this method, you must supply molecular structure. You can list the functional groups for the

Fedors method using the **Components | Molecular Structure | Functional Group** sheet.

The Fedors method is simple to use because it requires only the molecular structure, but is less accurate than the other methods such as the Joback method.

Gani

The Gani method uses contributions from both first-order and second-order groups. The second order groups account for the effect of neighboring atoms. Use of second order groups results in higher accuracy (*AIChE J*. 40,1697,1994).

The Gani method can be used to estimate: TB, TC, PC, VC, DHFORM, DGFORM, and DHVL. To use this method, you must supply molecular structure on the **Components | Molecular Structure | General** sheet. You can also list the functional groups using the **Functional Group** sheet.

For TB, the Gani method is more accurate than the Joback method. The error is about 2/5 of that of the Joback method.

For TC, PC, and VC, the Gani method is quite accurate. The authors tested approximately 400 organic compounds. The errors are summarized below:

Parameter	No. of Compounds	Avg. Relative Error(%)	Avg. Error
TC	400	0.85	4.8 5(K)
PC	390	2.89	1.13 (bar)
VC	310	1.79	6.0(cc/mol)

For DHFORM and DGFORM the Gani method is applicable to a wide range of compounds. It is straightforward to use. It is more accurate than the Joback method, but is less accurate than the Benson method. The reported average error for DHFORM and DGFORM are 3.71 kJ/mol and 3.24 kJ/mol, respectively.

For DHVL, the Gani method is used to estimate heat of vaporization at 298K, then the Watson equation is used to extrapolate heat of vaporization to TC.

Gunn-Yamada

The Gunn-Yamada method can be used to estimate liquid molar volume. To use this method, you must supply critical temperature, critical pressure, and the acentric factor.

The Gunn-Yamada method is used to estimate saturated liquid molar volume when the reduced temperature is less than 0.99. This method is applicable to nonpolar and slightly polar compounds. The calculated values are used to determine the Rackett parameter, RKTZRA. This method is more accurate than the Le Bas method and is recommended.

Helgeson

The Helgeson method is the only method available for estimating the Born coefficient of aqueous species (OMEGHG) for the Helgeson electrolyte model. This method requires S25HG and CHARGE as input.

Hg-aqu

The HG-AQU method estimates the Helgeson capacity parameters (CHGPAR) from the infinite dilution heat capacity CPAQ0.

Hg-cris

The HG-CRIS method estimates the Helgeson capacity parameters (CHGPAR) according to the Criss-Cobble method.

Hg-est

The HG-EST method estimates the Helgeson capacity parameters (CHGPAR) using an empirical relation developed by Aspen Technology.

Joback

The Joback method can be used to estimate: TB, TC, PC, VC, DHFORM, DGFORM, and CPIG. To use this method, you must supply molecular structure for estimating TB, PC, VC, DHFORM, DGFORM, and CPIG; you must supply molecular structure and normal boiling point for estimating TC. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

For TB, the Joback method gives only approximate estimate of normal boiling point. However, it is applicable to a wider range of compounds than the Ogata-Tsuchida method. The author reported average absolute error of 12.9 K for 408 diverse organic compounds.

For TC, PC, and VC, the Joback method is the best method to use overall. It is a modification of the Lydersen method using a larger data base. A few functional groups have also been removed. Joback tested approximately 400 organic compounds. The errors are summarized below:

Parameter	No. of Compounds	Avg. Relative Error(%)	Avg. Error
TC	400	0.8	4.8 (K)
PC	390	5.2	(2.1 (bar)
VC	310	2.3	7.5 (cc/mol)

For DHFORM, the Joback method is applicable to a wide range of compounds. It is straightforward to use, but is less accurate than the Benson method. The reported average error is 8.9 kJ/mol.

For DGFORM, the Joback method is applicable to a wide range of compounds. The reported errors are in the range of 5 to 10 kJ/mol. For complex materials, the errors are larger.

For CPIG, the Joback method is applicable to a wide range of compounds. It is easier to use than the Benson method, but is less accurate. The reported average error is 1.4% for 28 diverse components. It should not be used outside the temperature range of 280 to 1100 K.

Le Bas

The Le Bas method can be used to estimate liquid molar volume. To use this method, you must supply molecular structure. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

The Le Bas method is used to estimate liquid molar volume at TB. The result is used to determine the Rackett parameter, RKTZRA. For 29 diverse compounds, an average error of 3.9% has been reported.

Lee-Kesler

The Lee-Kesler method can be used to estimate the acentric factor. To use this method, you must supply normal boiling point, critical temperature, and critical pressure.

The Lee-Kesler method is recommended for hydrocarbons. The authors reported that this method yields values of acentric factor very close to those selected by Passut and Danner (Ind. Eng. Chem. Process Des. Dev. 12, 365, 1973).

Letsou-Stiel

The Letsou-Stiel method can be used to estimate liquid viscosity. To use this method, you must supply molecular weight, critical temperature, critical pressure, and the acentric factor.

The Letsou-Stiel method is applicable at high temperatures – for reduced temperatures of 0.76 to 0.92. The authors reported an average error of 3% for 14 liquids.

Li-Ma

The Li-Ma method is a group contribution method for estimating vapor pressure, heat of vaporization, and liquid surface tension.

For vapor pressure, the estimated parameters are valid from TB to TC. This method is accurate for polar and nonpolar compounds. For 28 diverse compounds, the reported average error was 0.61% (*Fluid Phase Equilibria*, 101, 101, 1994).

For heat of vaporization, the method requires molecular structure and TB as input. Reported average error for 400 diverse compounds was 1.05% (*Fluid Phase Equilibria*, 1997).

For surface tension, the method requires molecular structure and TB as input. Reported average error for 427 diverse compounds was 1.09% (*Fluid Phase Equilibria*, 118, 13, 1996).

Lydersen

The Lydersen method can be used to estimate: TC, PC, and VC. To estimate TC, you must supply molecular structure and normal boiling point. To estimate PC, you must supply molecular structure and molecular weight. For VC, you must supply molecular structure. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

The Lydersen method is one of the first successful methods for estimating critical parameters. The functional groups are almost identical to those for the Joback method. The estimated error for TC is usually less than 2%. For high molecular weight nonpolar compounds (MW > 100), the errors are 5% or higher. For PC and VC, the errors are approximately 4%.

Mani

The Mani method was developed by Juan-Carlos Mani of Aspen Technology. This method estimates TB from the Riedel equation when one or two experimental vapor pressure data points are available. This method can also be used to estimate TC and vapor pressure.

This method provides very accurate and reliable estimates of TB, TC and vapor pressure curve when some experimental vapor pressure data is available. It is very useful for complex compounds that decompose at temperatures below the normal boiling points.

McLeod-Sugden

The McLeod-Sugden method can be used to estimate surface tension. To use this method, you must supply normal boiling point, critical temperature, critical pressure, liquid molar volume, and Parachor parameters.

The McLeod-Sugden method is applicable to nonpolar, polar, as well as hydrogen-bonded liquids. For hydrogen-bonded liquids, errors are normally less than 5 to 10%.

Mostafa

The Mostafa method is a group contribution method for estimating solid standard Gibbs free energy of formation (DGSFRM), solid standard enthalpy of formation (DHSFRM), and parameters for the solid heat capacity correlation (CPSPO1).

This method is applied to solid inorganic salts which are divided to cations, anions and ligands. For DHSFRM, the reported average errors for 664 diverse solid inorganic salts, was 3.18% (*Ind. Eng. Chem. RES.*, 35, 343, 1996). For DGSFRM, the reported average errors for 687 diverse solid inorganic salts was 2.06% (*Ind. Eng. Chem. RES.*, 34, 4577, 1995).

Ogata-Tsuchida

The Ogata-Tsuchida method can be used to estimate normal boiling point. To use this method, you must supply molecular structure. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

The Ogata-Tsuchida method is applicable only to compounds with a single functional group, such as -OH and a single radical type, such as methyl. The authors tested 600 components and reported that 80% of the TBs were predicted within 2 K, 89% were within 3 K, and 98% were within 5 K. Deviations larger than 5 K were generally for compounds containing the methyl radical.

When the Ogata-Tsuchida method is applicable, it is more accurate than the Joback method.

Orrick-Erbar

The Orrick-Erbar method can be used to estimate liquid viscosity. To use this method, you must supply molecular structure, molecular weight, liquid molar volume, critical temperature, and critical pressure. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

The Orrick-Erbar method is limited to low temperatures, ranging from above the freezing point to the reduced temperature of 0.75. This method is not reliable for highly branched structures. It is not applicable to inorganic liquids or sulfur compounds. The authors reported an average error of 15% for 188 organic liquids.

Parachor

The Parachor method can be used to estimate the PARC parameter. This method requires molecular structure. Although Parachor is not required in any Aspen Physical Property System models, it is used in the McLeod-Sugden method to estimate surface tension.

Reichenberg

The Reichenberg method can be used to estimate vapor viscosity. To use this method, you must supply molecular structure, molecular weight, critical temperature, and critical pressure. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

For nonpolar compounds, the expected error is between 1 and 3%. For polar compounds, the errors are higher, but usually less than 4%.

Riedel

The Riedel method can be used to estimate vapor pressure and critical volume. To use this method, you must supply TB, TC, and PC.

For vapor pressure, the Riedel method is the only estimation method available. The Data method simply fits the experimental vapor pressure data you supply on the **Data | Pure Component** forms.

The Riedel method determines the vapor pressure parameters, PLXANT, that are valid from TB to TC. It is accurate for nonpolar compounds and not as accurate for polar compounds.

For VC, the Riedel method is recommended for hydrocarbons only.

Ruzicka

The Ruzicka method is a group contribution method for estimating parameters for the DIPPR liquid heat capacity correlation. The parameters are valid from the melting point to the normal boiling point. This method requires only molecular structure as input. For 9772 diverse compounds, reported average errors were 1.9% and 2.9% for nonpolar and polar compounds, respectively (*J. Phys. Chem. Ref. Data*, 22, 597, 1993; 22, 619, 1993).

Sato-Riedel

The Sato-Riedel method can be used to estimate liquid thermal conductivity. To use this method, you must supply molecular weight, normal boiling point, and critical temperature.

The Sato-Riedel method ranges widely in accuracy from 1 to 20% for the compounds tested. The accuracy is poor for light and branched hydrocarbons.

Simple

Use the Simple method to estimate TC. It does not depend on molecular structure, but requires MW and TB as input. This method was derived by Klincewicz and Reid. The average error for about 200 diverse organic compounds tested is 2.3% The Simple method is simple to use, but is less accurate than other methods such as the Joback method.

Thermo

The Thermo method can estimate standard enthalpy of formation of aqueous species (DHAQHG), standard Gibbs free energy of formation of aqueous species (DGAQHG), and absolute entropy of aqueous species (S25HG) for the Helgeson electrolyte model.

This method estimates the parameters according to thermodynamic relationship if the required data exist in the databank, as follows:

- DHAQHG = DGAQFM + 298.15 × (S025C – S025E)
- DGAQHG = DHAQFM – 298.15 × (S025C – S025E)
- S25HG = (DHAQFM – DGAQFM) / (298.15 + S025E)

where S025E is the sum of absolute entropy of the constituent elements of a compound at 25 °C.

Unifac

The UNIFAC method can be used to estimate binary parameters for the Wilson, NRTL, and UNIQUAC activity coefficient models. To use this method, you must supply molecular structure and the UNIFAC R and Q parameters for the functional groups. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

The UNIFAC method is applicable to a wide variety of components. It is valid in the temperature range of 20 to 150 deg C. It should not be used for light gases such as Hydrogen, Nitrogen, Oxygen, etc.

The UNIFAC method is used to generate activity coefficients at infinite dilution which is then used to determine the binary parameters for the Wilson, NRTL or UNIQUAC models. The infinite dilution activity coefficients predicted using UNIFAC may not be very accurate.

The UNIF-R4 method is UNIFAC using the revision 4 parameter set. UNIFAC is recommended; UNIF-R4 is provided for compatibility with very old versions of Aspen Plus.

Unifac-Dortmund

This is the modified Dortmund UNIFAC method. It can be used to estimate binary parameters for the Wilson, NRTL, and UNIQUAC activity coefficient models.

To use this method, you must supply molecular structure and the R and Q parameters for the functional groups. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

The UNIF-DMD method is used to generate activity coefficients at infinite dilution which is then used to determine the binary parameters for the Wilson, NRTL or UNIQUAC models.

The UNIF-DMD method is applicable non-electrolyte components with normal boiling points above 20 C. It is more accurate than the other UNIFAC based methods for estimating infinite dilution activity coefficients and is recommended.

Unifac-Lyngby

This is the modified Lyngby UNIFAC method. It can be used to estimate binary parameters for the Wilson, NRTL, and UNIQUAC activity coefficient models.

To use this method, you must supply molecular structure and the R and Q parameters for the functional groups. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

The UNIF-LBY method is used to generate activity coefficients at infinite dilution which is then used to determine the binary parameters for the Wilson, NRTL or UNIQUAC models.

The UNIF-LBY method is applicable non-electrolyte components with normal boiling points above 20 C.

Unifac-LL

This is the UNIFAC method with liquid-liquid data set. It can be used to estimate binary parameters for the Wilson, NRTL, and UNIQUAC activity coefficient models, although, it is not recommended for the Wilson model. Use this method when you want to use the binary parameters for liquid-liquid equilibrium calculations.

To use this method, you must supply molecular structure and the UNIFAC R and Q parameters for the functional groups. You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

The UNIF-LL method is applicable non-electrolyte components with normal boiling points above 20 C. It is valid in the temperature range of 20 to 40 deg C. It should not be used for light gases such as Hydrogen, Nitrogen, Oxygen, etc.

The UNIF-LL method is used to generate activity coefficients at infinite dilution which is then used to determine the binary parameters for the Wilson, NRTL or UNIQUAC models. The infinite dilution activity coefficients predicted using UNIF-LL may not be very accurate.

van Krevelen

The van Krevelen group contribution method is used to estimate property parameters for polymer segments. The parameters estimated are for the van Krevelen polynomial models for liquid and solid enthalpy, liquid and solid Gibbs free energy, liquid and solid density, glass transition temperature, and melt transition temperature. To use this method, you must supply molecular structure of the polymer segments in terms of van Krevelen functional groups. If the segment you would like to estimate parameters for is in the SEGPCD databank, you do not need to provide the structural information.

You can list the functional groups for this method using the **Components | Molecular Structure | Functional Group** sheet.

Vetere

The Vetere method can be used to estimate heat of vaporization. To use this method, you must supply molecular weight and normal boiling point.

The Vetere method is used to estimate heat of vaporization at TB. The Watson equation is then used to extrapolate heat of vaporization to TC. At TB, an average error of 1.6% has been reported.

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