Aspen Physical Property System

Physical Property Methods and Models 11.1

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About This Manual

Physical Property Methods and Models provides an overview of Aspen Plus physical property methods and detailed technical reference information on property option sets, property calculation methods and routes, property models, and parameter estimation. This volume also includes technical reference information for handling physical properties in electrolytes simulations, rigorous and three-phase calculations, and petroleum components characterization methods. Much of this information is also available in online prompts and help.

For information and listings for all Aspen Plus databanks, electrolytes data, group contribution method functional groups, and property sets, see *Aspen Plus Physical Property Data*.

An overview of the Aspen Plus physical property system, and information about how to use its full range and power, is in the *Aspen Plus User Guide*, as well as in online help and prompts in Aspen Plus.

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For More Information

Online Help   The Aspen Physical Property System has a complete system of online help and context-sensitive prompts. The help system contains both context-sensitive help and reference information.

Physical Property Reference Manuals   Aspen Physical Property System reference manuals provide detailed technical reference information about the physical property calculation system supplied with Aspen Plus and Aspen Properties.

Aspen Plus and Aspen Properties manuals   Aspen Plus reference manuals provide background information about Aspen Plus and Aspen Properties.

The manuals are delivered in Adobe portable document format (PDF).

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Overview of Aspen Physical Property Methods

Overview

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. Chapter 2 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 the Chapters 3 and 4.

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:

$$f_i^v = f_i^l \tag{1}$$

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:

$$f_i^v = \varphi_i^v y_i p \tag{2}$$

$$f_i^l = \varphi_i^l x_i p \tag{3}$$

With:

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

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:

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

$$f_i^l \qquad = \qquad x_i \gamma_i f_i^{*,l} \qquad\qquad\qquad (6)$$

Where φ_i^v is calculated according to equation 4,

$\gamma_i \qquad = \qquad$ Liquid activity coefficient of component i

$f_i^{*,l} \qquad = \qquad$ 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.

Equation-of-State Method

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

$$p_i = y_i p \qquad\qquad\qquad (7)$$

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:

$$f_i^v = \varphi_i^v y_i p \qquad\qquad\qquad (8)$$

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:

$$f_i^l = \varphi_i^l x_i p \qquad\qquad\qquad (9)$$

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

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, 0.2, 0.4, 0.6, 0.8 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 the pressure maximum of the phase envelope (cricondenbar). This is not a general rule.

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).
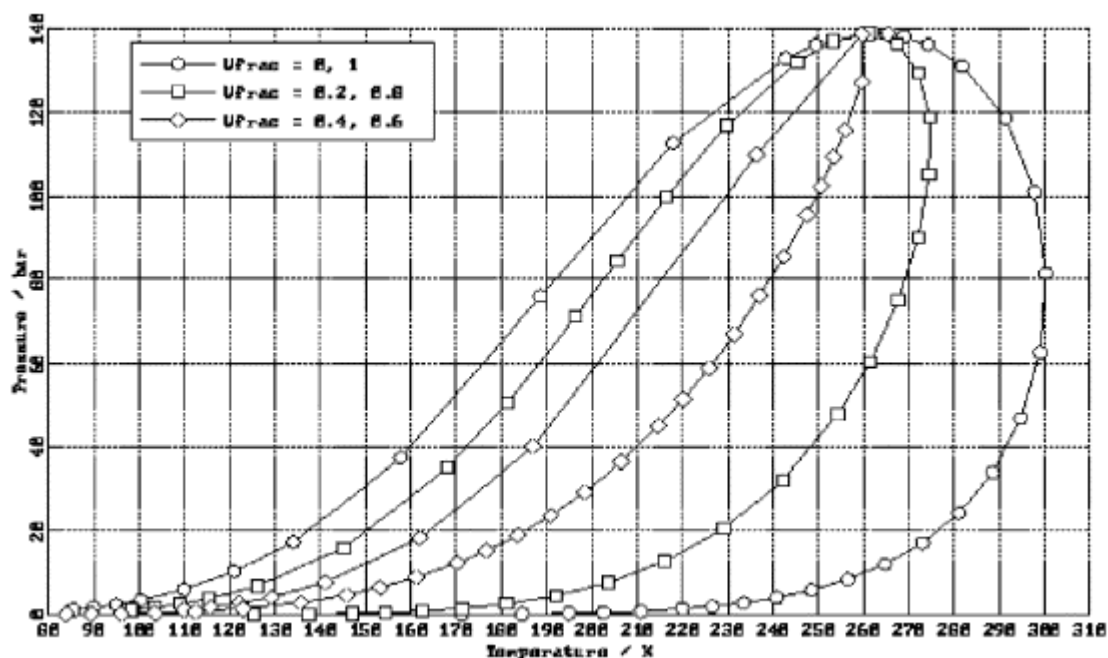
Phase Envelope of a Methane-Rich Hydrocarbon Mixture

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 0.75 (110 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

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:

$$\varphi_i^{l1} x_i^{l1} = \varphi_i^{l2} x_i^{l2} \tag{11}$$

and also to liquid-liquid-vapor equilibria:

$$\varphi_i^{v} y_i = \varphi_i^{l1} x_i^{l1} = \varphi_i^{l2} x_i^{l2} \tag{12}$$

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:

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

- 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:

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

- 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:

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

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:

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

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

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

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

Vapor and liquid volume is computed by solving $p(T,Vm)$ for Vm 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.

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 (ethyleneglycol) 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   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 this definition γ_i approaches unity as x_i approaches unity.

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

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

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

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:

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

Where:

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

By this definition γ_i^* 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

The basic liquid-liquid-vapor equilibrium relationship is:

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

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:

$$x_i^{l1}\gamma_i^{l1} = x_i^{l2}\gamma_i^{l2} \qquad (32)$$

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 the Aspen Plus User Guide, Chapter 31 or Aspen Properties User Guide 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.
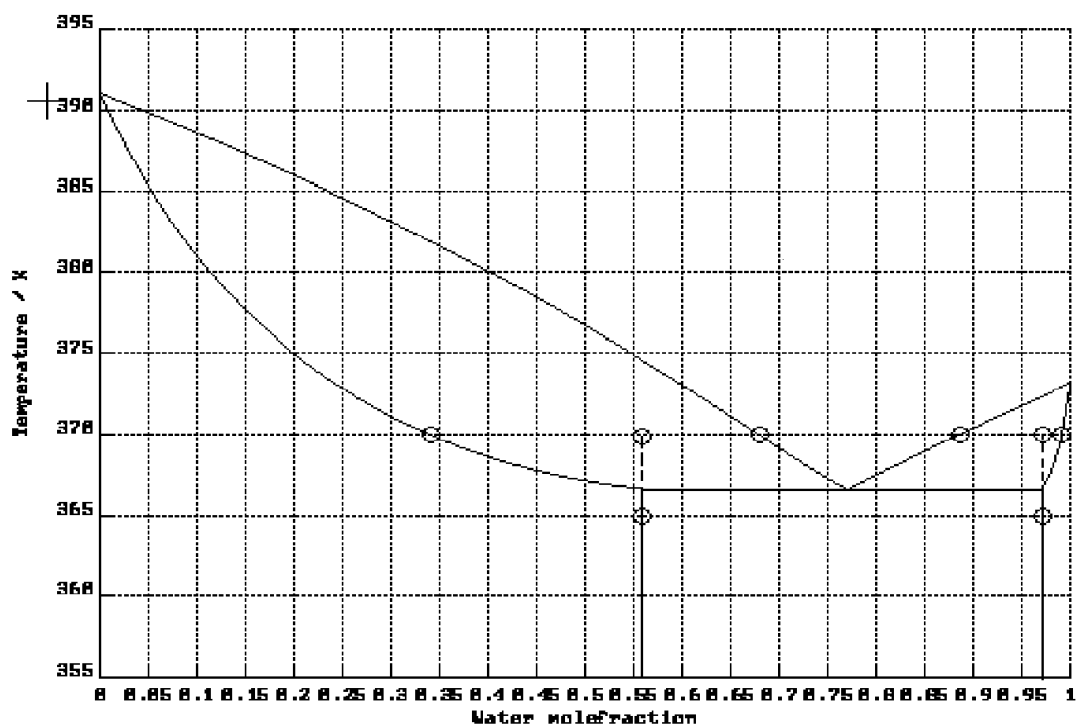
(T,x,x,y)—Diagram of Water and Butanol-1 at 1.01325 bar

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.
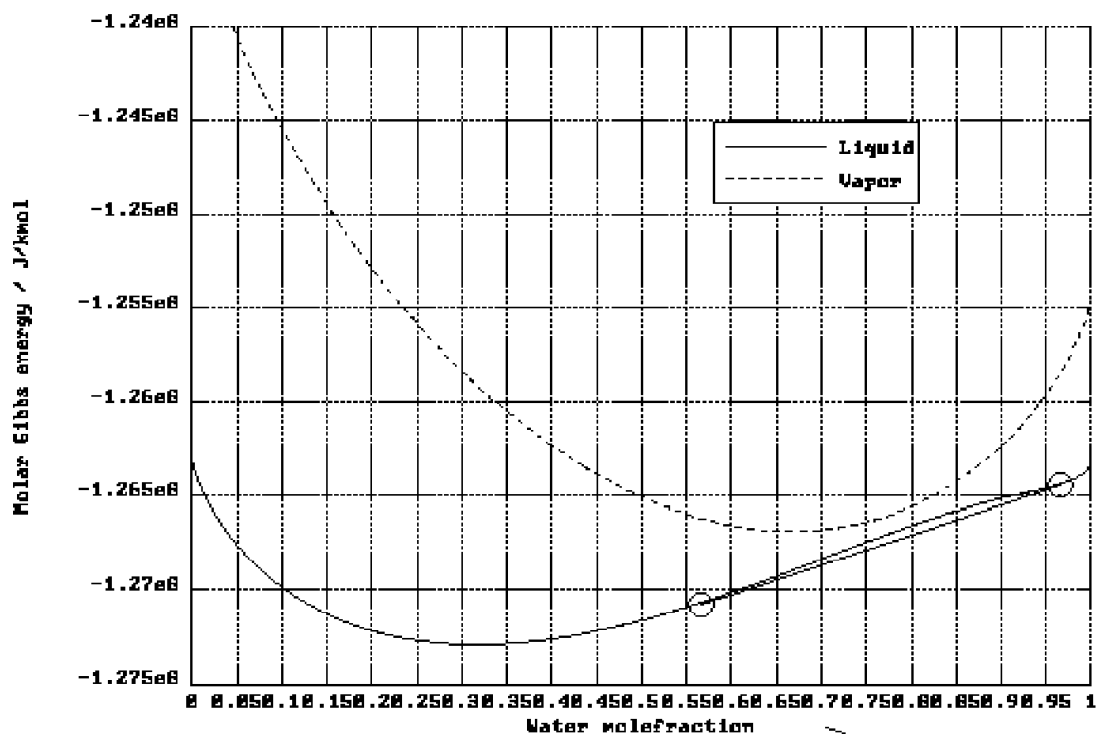
Molar Gibbs Energy of Butanol-1 and Water at 365 K and 1 atm
The Gibbs energy has been transformed by a contribution linear in the mole fraction, such that the Gibbs energy of pure liquid water (thermodynamic potential of water) has been shifted to the value of pure liquid n-butanol. This is done to 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.
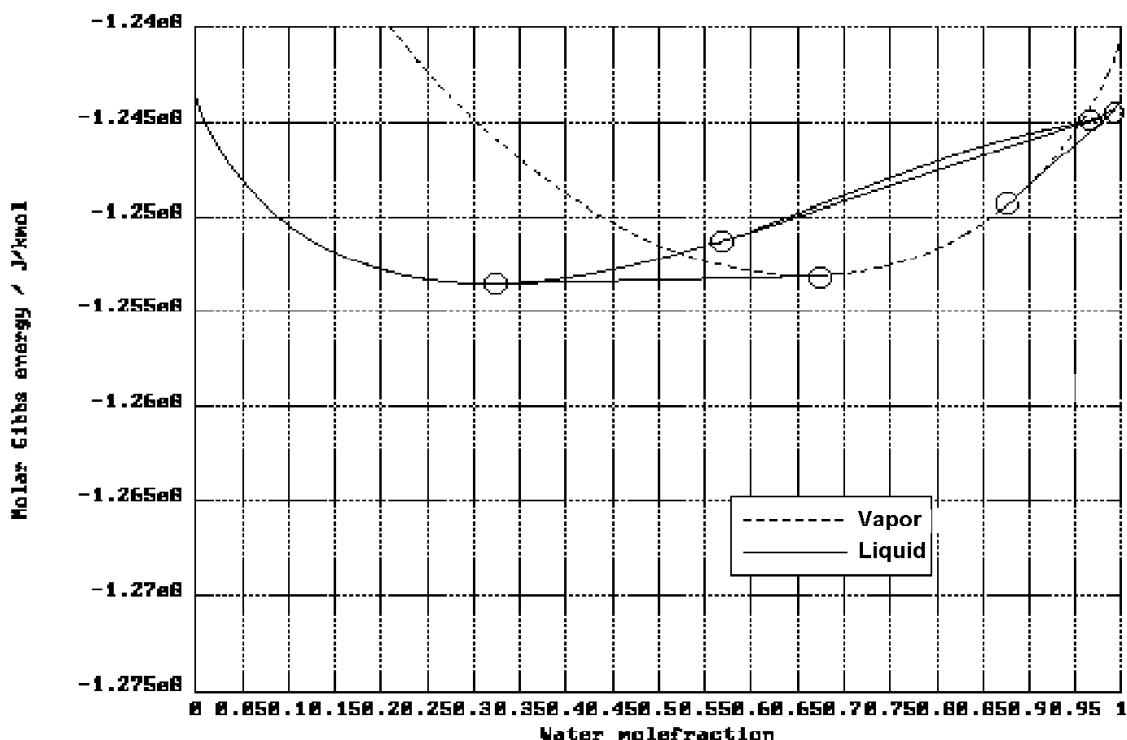
Molar Gibbs Energy of Butanol-1 and Water at 370 K and 1 atm

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 are stored in separate substreams.

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 Chapter 5). 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 Reactions Chemistry Equilibrium Constants sheet.

Salt precipitation is only calculated when the component is declared as a Salt on the Reactions 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 on page 1-Liquid-Liquid and Liquid-Liquid-Vapor Equilibria)

As a result, the analog of equation 31 holds:

$$x_i^{l1}\gamma_i^{l1}f_i^{*,l} = x_i^{l2}\gamma_i^{l2}f_i^{*,l} = ... x_i^{s1}\gamma_i^{s1}f_i^{*,s} = x_i^{s2}\gamma_i^{s2}f_i^{*,s} = ...\varphi_i^v y_i p \quad (33)$$

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.
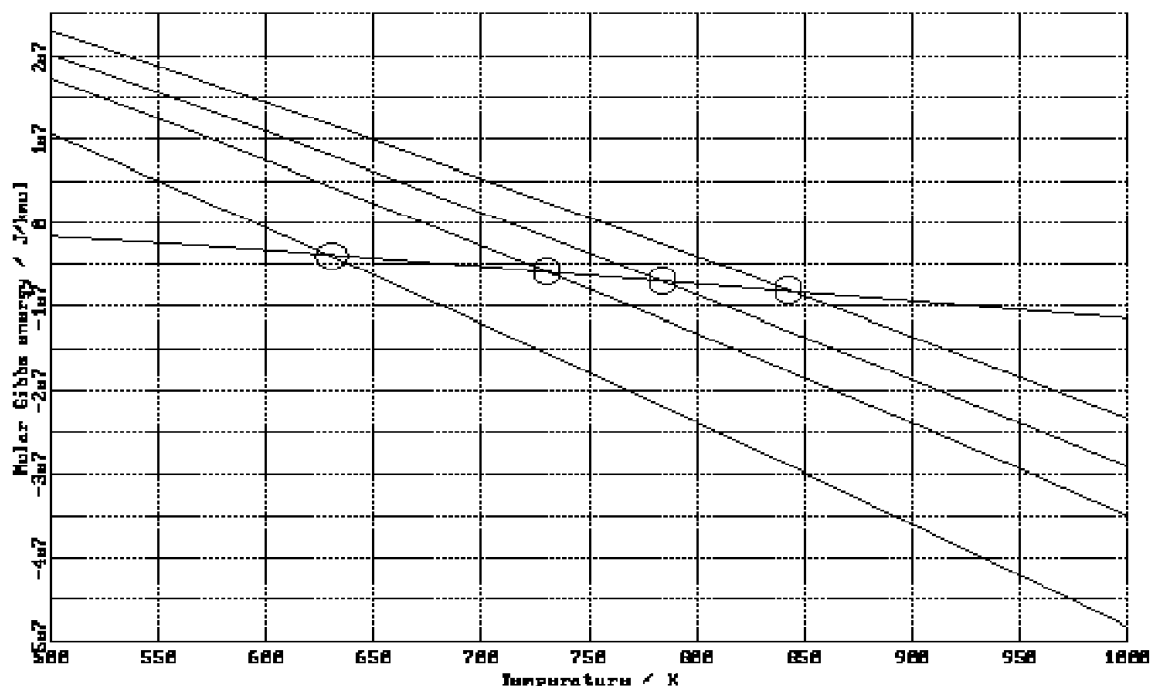
Thermodynamic Potential of Mercury at 1, 5, 10, and 20 bar
The pure component molar Gibbs energy is equal to the pure component thermodynamic potential. The ISO and IUPAC recommendation to use the thermodynamic potential is followed.
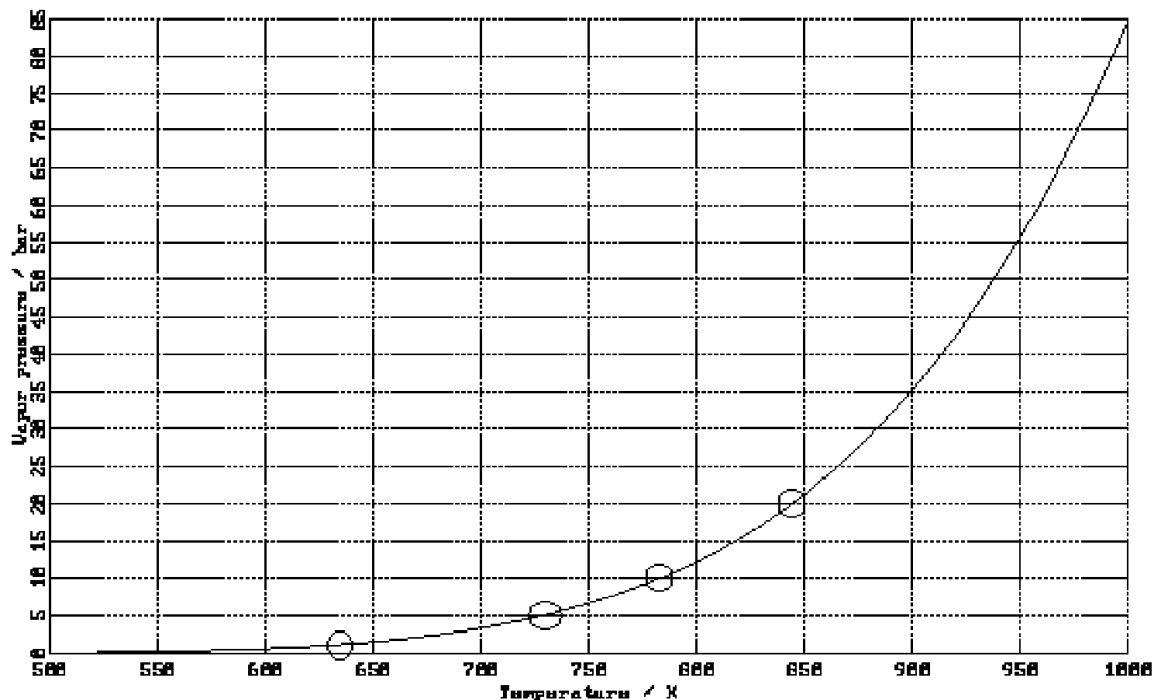
Vapor Pressure Curve of Liquid Mercury

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 Chapter 3).

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.

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:

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

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

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:

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

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 Physical Property Data, Chapter 1, 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:

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

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 $\dfrac{1}{r^6}$, with *r* being the distance between molecules.

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

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

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 this chapter). 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
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:

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

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

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:

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

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.

Virial Equations of State   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 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:

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

(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,

$$2A \leftrightarrow A_2 \qquad (50)$$

in the vapor phase is defined in terms of fugacities:

$$K = \frac{f_{A_2}}{f_A^2} \qquad (51)$$

With:

$$f_i^v = \varphi_i^v y_i p \qquad (52)$$

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

$$K = \frac{y_{A_2}}{y_A^2 p} \qquad (53)$$

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 Chapter 5).

K in equation 53 is only a function of temperature. If the pressure approaches zero at constant temperature, $\dfrac{y_{A_2}}{y_A^2}$,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 $\frac{1}{T}$ is approximately a straight line with a positive slope (since the reaction is exothermic) with increasing $\frac{1}{T}$. 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):

$$\varphi_i^{a,v} = \varphi_i^{t,v} \frac{y_i^t}{y_i^a} \tag{56}$$
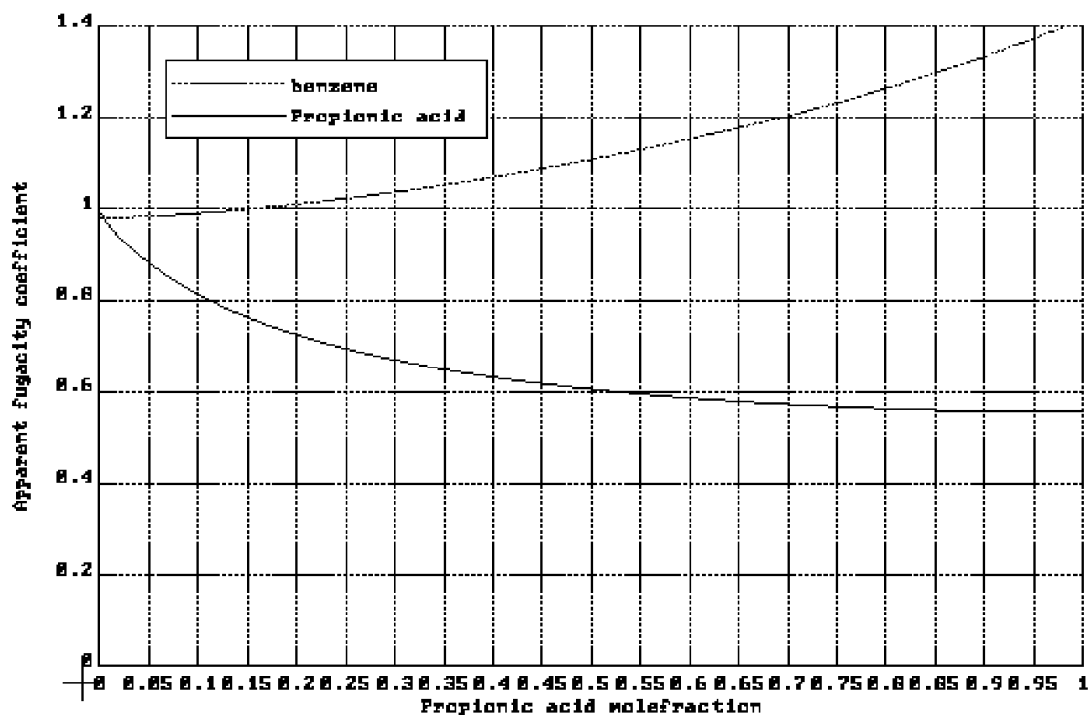
Apparent Fugacity of Vapor Benzene and Propionic Acid

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:

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

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.
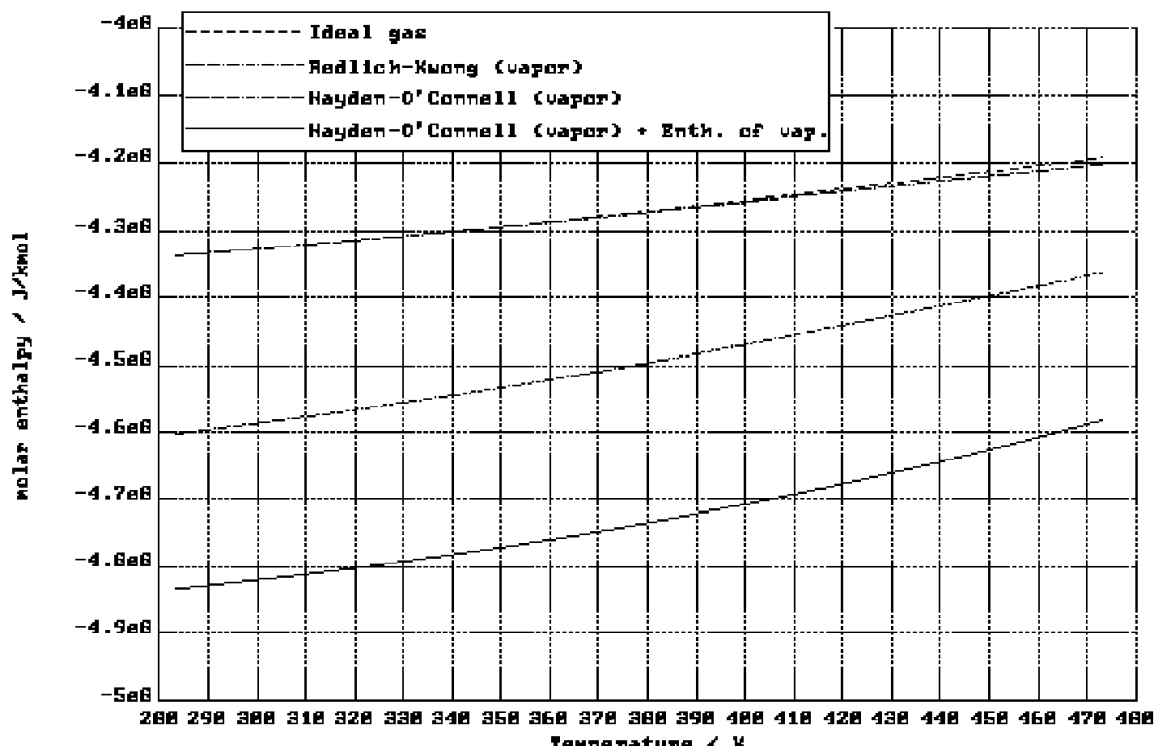
Liquid and Vapor Enthalpy of Acetic Acid

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 Nothagel and the Hayden-O'Connel 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 Chapter 3, UNIFAC, UNIFAC (Dortmund Modified), UNIFAC (Lyngby Modified).

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 Chapter 3, Electrolyte NRTL Activity Coefficient Model, Bromley-Pitzer Activity Coefficient Model, and Pitzer Activity Coefficient Model, and Appendices A, B, and C.

The Pitzer electrolyte activity coefficient model can be used for the representation of aqueous electrolyte solutions up to 6 molal strength (literature references in appendix C). 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 in appendix B). 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, Chapter 1). 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 in appendix A). 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 Chapman-Enskog-Brokaw and the Chung-Lee-Starling low pressure vapor viscosity models and the Stiel-Thodos 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:

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

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: Andrade/DIPPR for liquid viscosity and Sato-Riedel for 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

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

Surface tension is calculated by empirical, correlative models such as Hakim-Steinberg-Stiel/DIPPR. 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. The enthalpy is calculated as:

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

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:

$$\Delta_f h^s = \Delta_c h^s + \Delta_f h_{cp}^s \tag{60}$$

$\Delta_f h_{cp}^s$ 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 Chapter 3). This approach is recommended for computing DHFGEN for the ENTHGEN model.

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

Superscripts	Definitions
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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Property Method Descriptions

Overview

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

- Classification of property methods
- 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 Chapter 4.

Classification of Property Methods and Recommended Use

A property method is a collection of property calculation routes. (For more on routes, see Chapter 4). 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 Aspen Plus User Guide, Chapter 7).

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
- 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 in this chapter for more detailed recommendations. See Chapter 3 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 Aspen Plus User Guide, Chapter 7.

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
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 kij)
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
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
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 kij)
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	Equations of state for high pressure hydrocarbon applications (with combustion databank)
Coal	(and assay analysis with coal correlations)
Oil	(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 kij 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

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 Properties Parameters Binary Interaction form (HENRY-1) 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	Ideal gas heat capacity	CPIG or CPIGDP
Density	Ideal gas law	
Liquid mixture	Ideal liquid activity coefficient	
Fugacity coefficient		
	Extended Antoine 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	Watson/DIPPR	TC, (DHVLWT or DHVLDP)
Density	Rackett	TC, PC, (VC or VCRKT), (ZC or RKTZRA)

Transport Properties

Properties	Models	Parameter Requirements
Vapor mixture		
Viscosity	Chapman-Enskog-Brokaw/ DIPPR	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal conductivity	Stiel-Thodos low pres./ DIPPR	MW or KVDIP
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	Hakim-Steinberg-Stiel/ DIPPR	(TC, PC, OMEGA) or SIGDIP
Liquid mixture		
Viscosity	Andrade/DIPPR	MULAND or MULDIP
Thermal conductivity	Sato-Riedel/DIPPR	(MW, TC, TB) or KLDIP
Diffusivity	Wilke-Chan	MW, VB

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 Property Method (see PENG-ROB), and 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 Chapter 3.

Property Methods for Petroleum Mixtures

Liquid Fugacity and K-Value Models

Property Method Name	Models
BK10	Braun K10 K-value model
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
PENG-ROB	Peng-Robinson
RK-SOAVE	Redlich-Kwong-Soave
SRK	Soave-Redlich-Kwong

Common Models for Property Methods for Petroleum Mixtures

Property	Model
Liquid enthalpy	Lee-Kesler
Liquid molar volume	API
Vapor viscosity	Chapman-Enskog-Brokaw
Vapor thermal conductivity	Stiel-Thodos/DIPPR
Vapor diffusivity	Dawson-Khoury-Kobayashi
Surface tension	API surface tension
Liquid viscosity	API
Liquid thermal conductivity	Sato-Riedel/DIPPR
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.

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	Ideal gas heat capacity, Redlich-Kwong	CPIG or CPIGDP 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

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	Ideal gas heat capacity, Redlich-Kwong	CPIG or CPIGDP 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

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

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.

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:

- 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 Properties Parameters Binary Interaction PRKIJ-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 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.

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.

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	Ideal gas heat capacity, Peng-Robinson	TCPR or TC; PCPR or PC; OMGPR or OMEGA CPIG or CPIGDP
Liquid mixture		
Fugacity coefficient	Peng-Robinson	TCPR or TC; PCPR or PC; OMGPR or OMEGA CPIG or CPIGDP
Enthalpy, entropy, Gibbs free energy	Ideal gas heat capacity, Peng-Robinson	TCPR or TC; PCPR or PC; OMGPR or OMEGA CPIG or CPIGDP

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 Rackett 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, RKSKIJ, 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 Properties Parameters Binary Interaction RKSKIJ-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	Ideal gas heat capacity, Redlich-Kwong-Soave	CPIG or CPIGDP, TC, PC, OMEGA
Liquid mixture		
Fugacity coefficient	Redlich-Kwong-Soave	TC, PC, OMEGA
Enthalpy, entropy, Gibbs free energy	Ideal gas heat capacity, Redlich-Kwong-Soave	CPIG or CPIGDP 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 enthalpy of water for better accuracy

- Kabadi-Danner mixing rules when dealing with water-hydrocarbon system

- Composition-independent fugacity coefficient for faster convergence in equation-based modeling

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 Ethylene 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. 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	Ideal gas heat capacity, Soave-Redlich-Kwong	(CPIG or CPIGDP) and SRKTC, SRKPC, SRKOMG
Liquid mixture		
Fugacity coefficient, Density	Soave-Redlich-Kwong	SRKTC, SRKPC, SRKOMG
Enthalpy, entropy, Gibbs free energy	Ideal gas heat capacity, Soave-Redlich-Kwong	(CPIG or CPIGDP) and SRKTC, SRKPC, SRKOMG

Common Models

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 of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Thermodynamic Properties

Property	Models	Parameter Requirements
Liquid mixture Enthalpy, Entropy	Ideal heat capacity, Lee-Kesler	(CPIG or CPIGDP) TC, PC, OMEGA
Density	Real components: Rackett	TC, PC, (VC or VCRKT), (ZC or RKTZRA)
	Pseudo components:	TB, API

Transport Properties

Property	Models	Paremeter Requirements
Vapor mixture Viscosity	Chapman-Enskog-Brokaw/ DIPPR	MW, (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal Conductivity	Stiel-Thodos/ DIPPR	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	Sato-Riedel/ DIPPR	(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 Chapter 1). 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 Properties 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	Ideal heat capacity, BWR-Lee-Starling	(CPIG or CPIGDP) and TC, VC, OMEGA
Liquid mixture		
Fugacity coefficient, Density	BWR-Lee-Starling	TC, VC, OMEGA
Enthalpy, Entropy, Gibbs energy	Ideal heat capacity, BWR-Lee-Starling	(CPIG or CPIGDP) and 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 $\rho_r = 3.0$. 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).

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	Ideal heat capacity, Benedict-Webb-Rubin-Starling	(CPIG or CPIGDP) and BWRSTC, BWRSVC, BWRSOM
Liquid mixture Fugacity coefficient, Density	Benedict-Webb-Rubin-Starling	BWRSTC, BWRSVC, BWRSOM
Enthalpy, Entropy, Gibbs energy	Ideal heat capacity, Benedict-Webb-Rubin-Starling	(CPIG or CPIGDP) and BWRSTC, BWRSVC, BWRSOM

K. E. Starling, "Fluid Themodynamic 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 Properties 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.

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture		
Fugacity coefficient, Density	Lee-Kesler-Plöcker	TC, PC, VC, OMEGA
Enthalpy, entropy Gibbs free energy	Ideal gas heat capacity, Lee-Kesler-Plöcker	(CPIG or CPIGDP) and 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	Ideal gas heat capacity, Lee-Kesler-Plöcker	(CPIG or CPIGDP) and 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.

Thermodynamic Properties	Models	Parameter Requirements
Vapor or liquid mixture		
Fugacity coefficient Density	Peng-Robinson	TCPR, PCPR, OMEGA
Enthalpy, entropy, Gibbs free energy	Ideal gas heat capacity, Peng-Robinson	CPIG or CPIGDP, 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 Aspen Physical Property System does not have built-in binary parameters for this property method.

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	Ideal gas heat capacity, Redlich-Kwong-Soave	CPIG or CPIGDP, TCRKS, PCRKS, OMGRKS

Common Models

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 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

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 coeffient 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 Chapter 3).

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 Chapter 4 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 Chapter 3.

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
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
Surface tension	Hakim-Steinberg-Stiel/DIPPR
Liquid viscosity	Chung-Lee-Starling
Thermal conductivity	Chung-Lee-Starling
Liquid diffusivity	Wilke-Chang liquid

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 Chapter 3.

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.

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture		
Fugacity coefficient, Density	Peng-Robinson-MHV2, UNIFAC	TC, PC, OMEGA, UFGRP, GMUFQ, GMUFR
Enthalpy, Entropy, Gibbs energy	Ideal heat capacity, Peng-Robinson-MHV2, UNIFAC	(CPIG or CPIGDP), TC, PC, OMEGA, 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 Chapter 3.

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, UNIFAC	TC, PC, OMEGA, UFGRP, GMUFR, GMUFQ
Enthalpy, Entropy, Gibbs energy	Ideal heat capacity, PengRobinson-WS, UNIFAC	(CPIG or CPIGDP),TC, PC, OMEGA, 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 Chapter 3.

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.

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture		
Fugacity coefficient, Density	PSRK, UNIFAC	TC, PC, OMEGA, UFGRP, GMUFR, GMUFQ
Enthalpy, Entropy, Gibbs energy	Ideal heat capacity, PSKR, UNIFAC	(CPIG or CPIGDP),TC, PC, OMEGA, 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. RKS-BM 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 Chapter 3.

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.

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	Ideal heat capacity, Redlich-Kwong-Aspen	(CPIG or CPIGDP) and 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 Chapter 3.

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.

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture		
Fugacity coefficient, Density	Redlich-Kwong-Soave-MHV2, Lyngby modified UNIFAC	TC, PC, OMEGA, UFGRPL, GMUFLR, GMUFLQ
Enthalpy, Entropy, Gibbs energy	Ideal heat capacity, Redlich-Kwong-Soave-MHV2, Lyngby modified UNIFAC	(CPIG or CPIGDP),TC, PC, OMEGA, 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 Chapter 3.

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.

Thermodynamic Properties	Models	Parameter Requirements
Vapor and liquid mixture		
Fugacity coefficient, Density	Redlich-Kwong-Soave-WS, UNIFAC	TC, PC, OMEGA, UFGRP, GMUFR, GMUFQ
Enthalpy, Entropy, Gibbs energy	Ideal heat capacity, Redlich-Kwong-Soave-WS, UNIFAC	(CPIG or CPIGDP),TC, PC, OMEGA, 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 extended Antoine 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 Chapter 3.

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	Ideal gas heat capacity/DIPPR Schwartzentruber-Renon	(CPIG or CPIGDP) Optional: RKUPPn, RKUCn, RKUKAn, RKULAn, RKUKBn n = 0, 1, 2

Common Models

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 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	Hakim-Steinberg-Stiel/ DIPPR	(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	Extended Antoine
Liquid molar volume	Rackett
Heat of vaporization	Watson
Vapor viscosity	Chapman-Enskog-Brokaw
Vapor thermal conductivity	Stiel-Thodos/DIPPR
Vapor diffusivity	Dawson-Khoury-Kobayashi
Surface tension	Hakim-Steinberg-Stiel/DIPPR
Liquid viscosity	Andrade/DIPPR
Liquid thermal conductivity	Sato-Riedel/DIPPR
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 Chapter 3.

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	Ideal heat capacity, Redlich-Kwong	(CPIG or CPIGDP), 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 (*bi*, *pi* and *di*). 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 Chapter 3.

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	Ideal heat capacity, Nothnagel	(CPIG or CPIGDP), 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 Chapter 3.

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	Ideal heat capacity, Hayden-O'Connell	(CPIG or CPIGDP), 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 Chapter 3.

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	VLE Reg	LLE Lit	LLE Reg	Henry Lit	Henry 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 Physical Property Data, Chapter 1.

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 Physical Property Data, Chapter 1).

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 Chapter 3.

Parameters Required for NRTL Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture		
Fugacity coefficient, Gibbs energy	NRTL liquid activity coefficient	NRTL
	Extended Antoine 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	Ideal gas heat capacity	CPIG or CPIGDP
	Watson/DIPPR heat of vaporization	TC, (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.

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	—

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. For details on the models, see Chapter 3.

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 Physical Property Data, Chapter 1).

The options 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 Physical Property Data, Chapter 3.

The minimum parameter requirements for the UNIFAC and modified UNIFAC models are given in the following table. For details about the models, see Chapter 3.

Parameters Required for the UNIFAC Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture		
Fugacity coefficient, Gibbs energy	UNIFAC	UFGRPD
	or:	
	Dortmund modified UNIFAC	UFGRPL
	or:	
	Lyngby modified UNIFAC	PLXANT
	Extended Antoine vapor pressure	Solvent: VC,
	Henry's constant	Solute-solvent: HENRY
	Brelvi-O'Connell	Solvent: TC, PC, (ZC or RKTZRA), Solute: (VC or VLBROC)
Enthalpy, Entropy	Ideal gas heat capacity	CPIG or CPIGDP
	Watson/DIPPR heat of vaporization	TC, (DHVLWT or DHVLDP)
	UNIFAC	UFGRP
	or:	
	Dortmund modified UNIFAC	UFGRPD
	or:	
	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

Binary Parameters

Property Method Name	Dataset Number	VLE Lit	VLE Reg	LLE Lit	LLE Reg	Henry Lit	Henry 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

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 *Physical Property Data*, Chapter 1).

You can model the solubility of supercritical gases using Henry's law. Henry coefficients are available from the databank (see *Physical Property Data*, Chapter 1).

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.

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 Chapter 3.

Parameters Required for UNIQUAC Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture		
Fugacity coefficient,		
Gibbs energy	UNIQUAC liquid activity coefficient	GMUQR, GMUQQ, UNIQ
	Extended Antoine 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	Ideal gas heat capacity	CPIG or CPIGDP
	Watson/DIPPR 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

Binary Parameters

Property Method Name	Dataset number	VLE Lit	VLE Reg	LLE Lit	LLE Reg	Henry Lit	Henry 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

The Van Laar model can describe nonideal liquid solutions with positive deviations from Raoult's law (see Chapter 1). 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 Physical Property Data, Chapter 1).

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 Chapter 3.

Parameters Required for Van Laar Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture		
Fugacity coefficient,		
Gibbs energy	Van Laar liquid activity coefficient	VANL
	Extended Antoine 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	Ideal gas heat capacity	CPIG or CPIGDP
	Watson/DIPPR 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 are listed in the following table.

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	—
WILS-GLR	1	—	—	—	—	X	X	Ideal Gas law	—
WILS-LR	1	—	—	—	—	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

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 Physical Property Data, Chapter 1).

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 Physical Property Data, Chapter 1).

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 Chapter 3.

Parameters Required for the Wilson Property Methods

Thermodynamic Properties	Models	Parameter Requirements
Liquid mixture		
Fugacity coefficient,		
Gibbs energy	Wilson liquid activity coefficient	WILSON
	Extended Antoine 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	Ideal gas heat capacity	CPIG or CPIGDP
	Watson/DIPPR heat of vaporization	TC, (DHVLWT or DHVLDP)
	Wilson liquid activity coefficient	WILSON
Density	Rackett	TC, PC, (VC or VCRKT), (ZC or RKTZRA)

Common Models

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 of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Transport Properties

Property	Models	Parameter Requirements
Vapor mixture		
Viscosity	Chapman-Enskog-Brokaw/ DIPPR	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal conductivity	Stiel-Thodos low pres./ DIPPR	MW or KVDIP
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	Hakim-Steinberg-Stiel/ DIPPR	(TC, PC, OMEGA) or SIGDIP
Liquid mixture		
Viscosity	Andrade/DIPPR	MULAND or MULDIP
Thermal Conductivity	Sato-Riedel/DIPPR	(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 ELECNRTL property method 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

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
PITZER	Pitzer	Redlich-Kwong-Soave
PITZ-HG	Pitzer	Redlich-Kwong-Soave
B-PITZER	Bromley-Pitzer	Redlich-Kwong-Soave

Common Models For Rigorous Property Methods

Property	Model
Vapor pressure	Extended Antoine
Liquid molar volume	Rackett/Clarke
Heat of vaporization	Watson/DIPPR
Infinite dilution heat capacity	Criss-Cobble
Vapor viscosity	Chapman-Enskog-Brokaw
Vapor thermal conductivity	Stiel-Thodos/DIPPR
Vapor diffusivity	Dawson-Khoury-Kobayashi
Surface tension	Hakim-Steinberg-Stiel/DIPPR - Onsager-Samara
Liquid viscosity	Andrade/DIPPR - Jones-Dole
Liquid thermal conductivity	Sato-Riedel/DIPPR - 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 Chapter 1. Chapter 5 contains specifics on electrolyte calculation. For details on methods, see Chapter 4. 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 Chapter 3.

AMINES

The AMINES property methoduses 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)	15 – 30	20 – 40	20 – 40	40 – 65

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 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	Ideal gas heat capacity/DIPPR	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
	Extended Antoine vapor pressure (amines and water only)	PLXANT
	Kent-Eisenberg (H2S and CO2 only)	—
Enthalpy, entropy	Watson heat of vaporization and DIPPR model	TC; PC;DHVLWT or DHVLDP
Density	Rackett molar volume	TC; PC: VC or VCRKT; ZC or RKTZRA

Transport Properties

Properties	Models	Parameter Requirements
Vapor mixture	Dean-Stiel	
Viscosity		MW; (MUP and (STKPAR or LJPAR)) or MUVDIP; TC, PC, VC
Thermal conductivity	Stiel-Thodos	MW, TC, PC, VC, ZC
Diffusivity	Dawson-Khoury-Kobayaski	MW; MUP and (STKPAR or LJPAR); VC
Surface tension	Hakim-Steinberg-Stiel/ DIPPR	(TC, PC, OMEGA) or SIGDIP
Liquid mixture		
Viscosity	Andrade/DIPPR	MULAND or MULDIP
Thermal Conductivity	Sato-Riedel/DIPPR	(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.

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 **Properties | Property 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 of reaction	DHFORM
Gibbs energy of reaction	DGFORM

Properties	Models	Parameter Requirements
Vapor mixture		
Viscosity	Chapman-Enskog-Brokaw/ DIPPR	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal conductivity	Stiel-Thodos low pres./ DIPPR	MW or KVDIP
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	Hakim-Steinberg-Stiel/ DIPPR	(TC, PC, OMEGA) or SIGDIP
Liquid mixture		
Viscosity	Andrade/DIPPR	MULAND or MULDIP
Thermal Conductivity	Sato-Riedel/DIPPR	(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 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 Physical Property Data, Chapter 2, 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 Chapter 1).

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 the 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 Chapter 3.

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	Ideal gas heat capacity/ DIPPR/ Barin 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
	Extended Antoine 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	Ideal gas heat capacity/ DIPPR and	CPIG or CPIGDP
	Watson/DIPPR 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	Solids heat capacity polynomial/ Barin correlation	CPSP01 or CPSXP1 to CPSXP7
Density	Solids molar volume polynomial	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 Chapter 3. 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 the ELECNRTL 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.

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.

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 Chapter 1).

You can model the solubility of supercritical gases using Henry's law. Henry coefficients are available from the Aspen Physical Property System databanks (see Chapter 1).

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 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 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 Chapter 3.

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	Ideal gas heat capacity/DIPPR/ Barin correlation	CPIG orCPIGDP or CPIXP1, CPIXP2, CPIXP3
	Redlich-Kwong	TC, PC, OMEGA
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
	Extended Antoine 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	Ideal gas heat capacity/DIPPR and	CPIG or CPIGDP
	Watson/DIPPR 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	Solids heat capacity polynomial/ Barin correlation	CPSP01 or CPSXP1 to CPSXP7
Density	Solids molar volume polynomial	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. But, 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 Chapter 1).

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 Chapter 3.

Parameters Required for the B-PITZER Property Method

Thermodynamic Properties	Models	Parameter Requirements
Vapor mixture		
Fugacity coefficient,		
Density	Redlich-Kwong-Soave	TC, PC, OMEGA
Enthalpy, Entropy, Gibbs energy	Ideal gas heat capacity/ DIPPR/ Barin correlation and	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
	Extended Antoine 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	Ideal gas heat capacity/DIPPR and	CPIG or CPIGDP
	Watson/DIPPR 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	Solids heat capacity polynomial/ Barin correlation	CPSP01 or CPSXP1 to CPSXP7
Density	Solids molar volume polynomial	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 Chapter 3.

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

Property	Models	Parameter Requirements
Vapor mixture		
Viscosity	Chapman-Enskog-Brokaw/ DIPPR	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal conductivity	Stiel-Thodos low pres./ DIPPR	MW or KVDIP
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	Hakim-Steinberg-Stiel/ DIPPR Onsager-Samaras †	Solv., Mol.sol.: (TC, PC, OMEGA) or SIGDIP Ion: CHARGE
Liquid mixture		
Viscosity	Andrade/DIPPR Jones-Dole †	Solv., Mol.sol.: MULAND or MULDIP Ion: IONMUB, IONMOB
Thermal Conductivity	Sato-Riedel/ DIPPR Riedel †	Solv., Mol.sol.: (MW, TC, TB) or KLDIP Ion: IONRDL
Diffusivity	Wilke-Chang/ Nernst-Hartley †	Solv., Mol.sol.: MW, VB Ion: CHARGE, IONMOB

† Only for rigorous electrolyte property methods

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 (for details on the use of substreams, see Aspen Plus User Guide, Chapter 9).

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 Aspen Plus User Guide, Chapter 7. Details on nonconventional property methods and models are given in chapters 1 and 3 of this manual, respectively.

When the solids are decomposed into individual components (for example, to selectively undergo chemical reactions), they 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.

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 Started Modeling 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 Chapter 3.

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

Property/Purpose	Parameter Requirements
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	
Enthalpy, Entropy, Gibbs energy	Ideal gas heat capacity/ DIPPR/ Barin correlation	CPIG or CPIGDP or CPIXP1, CPIXP2, CPIXP3
Density	Ideal gas law	
Liquid pure and mixture		
Fugacity Coefficient, Gibbs energy	Extended Antoine vapor pressure/ Barin correlation	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	[Ideal gas heat capacity/ DIPPR and	CPIG or CPIGDP
	Watson/DIPPR heat of vaporization	TC, (DHVLWT or DHVLDP)]
	DIPPR heat capacity correlation/ Barin correlation	(CPLDIP or CPLXP1, CPLXP2
Density	Constant Volume, Ideal mixing	VLCONS
Solid pure (and mixture)		
Fugacity Coefficient, Gibbs energy	Extended Antoine vapor pressure/ Barin correlation	PLXANT CPSXP1 to CPSXP7
	Ideal liquid activity coefficient	—
Enthalpy, Entropy	Solids heat capacity polynomial/ Barin correlation	CPSP01 or CPSXP1 to CPSXP7
Density	Solids molar volume polynomial	VSPOLY

Transport Properties

Property	Models	Parameter Requirements
Vapor pure and mixture		
Viscosity	Chapman-Enskog-Brokaw/ DIPPR	MW; (MUP and (STKPAR or LJPAR)) or MUVDIP
Thermal conductivity DIPPR	Stiel-Thodos low pres./ KVDIP	MW or
Diffusivity	Chapman-Enskog-Wilke-Lee	MW; MUP and (STKPAR or LJPAR)
Surface tension	Hakim-Steinberg-Stiel/ DIPPR	(TC, PC, OMEGA) or SIGDIP
Liquid pure and mixture		
Viscosity	Andrade/DIPPR	MULAND or MULDIP
Thermal Conductivity	Sato-Riedel/DIPPR	(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 two 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. The NBS/NRC steam tables are more recent and accurate.

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 and NBS/NRC Steam Tables in Chapter 3.

Steam Tables Property Methods

Property Method Name	Models
	Steam Tables:
STEAM-TA	ASME 1967
STEAMNBS/STMNBS2	NBS/NRC 1984
	Common models:
	IAPS vapor viscosity
	IAPS vapor thermal conductivity
	IAPS surface tension
	IAPS liquid viscosity
	IAPS liquid thermal conductivity

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.

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/STEAMNBS2

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 STMNBS2 method is recommended for use with the SRK, BWRS, MXBONNEL and GRAYSON2 property methods.

Property Model Descriptions

Overview

This chapter describes the property models available in the Aspen Physical Property System and defines the parameters used in each model. The description for each model lists the parameter names used to enter values on the Properties Parameters forms.

This chapter also lists the pure component temperature-dependent properties that the Aspen Physical Property System can calculate from a model that supports several equations or submodels. See Pure Component Temperature-Dependent Properties (below).

Many parameters have default values indicated in the Default column. A dash (–) indicates that the parameter has no default value and you must provide a value. If a parameter is missing, calculations stop. The lower limit and upper limit for each parameter, when available, indicate the reasonable bounds for the parameter. The limits are used to detect grossly erroneous parameter values.

The property models are divided into the following categories:

- Thermodynamic property models
- Transport property models
- Nonconventional solid property models

The property types for each category are discussed in separate sections of this chapter. The following table (below) provides an organizational overview of this chapter. The tables labeled Thermodynamic Property Models, Transport Property Models, and Nonconventional Solid Property Models in this chapter present detailed lists of models. These tables also list the Aspen Physical Property System model names, and their possible use in different phase types, for pure components and mixtures.

Electrolyte and conventional solid property models are presented in Thermodynamic Property Models, this chapter. For more details on electrolyte coefficient models, see Appendices A, B, and C.

Categories of Models

Category	Sections
Thermodynamic Property Models	Equation-of-State Models
	Activity Coefficient Models
	Vapor Pressure and Liquid Fugacity Models
	Heat of Vaporization Models
	Molar Volume and Density Models
	Heat Capacity Models
	Solubility Correlations
	Other
Transport Property Models	Viscosity Models
	Thermal Conductivity Models
	Diffusivity Models
	Surface Tension Models
Nonconventional Solid Property Models	General Enthalpy and Density Models
	Enthalpy and Density Models for Coal and Char

Pure Component Temperature-Dependent Properties

The following table lists the pure component temperature-dependent properties that the Aspen Physical Property System can calculate from a model that supports several equations or submodels.

For example, the Aspen Physical Property System can calculate heat of vaporization using these equations:

- Watson
- DIPPR
- PPDS
- IK-CAPE

Pure Component Temperature-Dependent Properties

Property	Submodel-Selection Parameter Element Number	Available Submodels	Default DIPPR Equation Number
Solid Volume	THRSWT/1	Aspen, DIPPR, PPDS, IK-CAPE	100
Liquid Volume	THRSWT/2	Aspen, DIPPR, PPDS, IK-CAPE	105/116
Liquid Vapor Pressure	THRSWT/3	Aspen, Wagner, BARIN, PPDS, IK-CAPE	101/115
Heat of Vaporization	THRSWT/4	Aspen, DIPPR, PPDS, IK-CAPE	106
Solid Heat Capacity	THRSWT/5	Aspen, DIPPR, BARIN, PPDS, IK-CAPE	100
Liquid Heat Capacity	THRSWT/6	DIPPR, PPDS, BARIN, IK-CAPE	100/114
Ideal Gas Heat Capacity	THRSWT/7	Aspen, DIPPR, BARIN, PPDS, IK-CAPE	107
Second Virial Coefficient	THRSWT/8	DIPPR	104
Liquid Viscosity	TRNSWT/1	Aspen, DIPPR, PPDS, IK-CAPE	101
Vapor Viscosity	TRNSWT/2	Aspen, DIPPR, PPDS, IK-CAPE	102
Liquid Thermal Conductivity	TRNSWT/3	Aspen, DIPPR, PPDS, IK-CAPE	100
Vapor Thermal Conductivity	TRNSWT/4	Aspen, DIPPR, PPDS, IK-CAPE	102
Liquid Surface Tension	TRNSWT/5	Aspen, DIPPR, PPDS, IK-CAPE	106

Which equation is actually used to calculate the property for a given component depends on which parameters are available. If parameters are available for more than one equation, the Aspen Physical Property System uses the parameters that were entered or retrieved first from the databanks. The selection of submodels is driven by the data hierarchy, and controlled by the submodel-selection parameters.

The thermodynamic properties use the THRSWT submodel-selection parameter, and the transport properties use the TRNSWT submodel-selection parameter.

As the previous table shows, a property is associated with an element of the parameter. For example, the Aspen Physical Property System uses THRSWT element 1 to select a submodel for solid volume.

The following table shows the values for THRSWT or TRNSWT, and the corresponding submodels.

Parameter Values (Equation Number)	Submodel
0	Aspen
1 to 116	DIPPR
200 to 211	BARIN
301 to 302	PPDS
401 to 404	IK-CAPE

All built-in databank components have model-selection parameters (THRSWT, TRNSWT) that are set to use the correct equations that are consistent with the available parameters. For example, suppose that parameters for the DIPPR equation 106 are available for liquid surface tension. For that component, TRNSWT element 5 is set to 106 in the databank. If you are retrieving data from an in-house or user databank, you should store the appropriate values for THRSWT and TRNSWT in the databank, using the appropriate equation number. Otherwise, the Aspen Physical Property System will search for the parameters needed for the Aspen form of the equations.

If a component is available in more than one databank, the Aspen Physical Property System uses the data and equations based on the databank list order on the Components Specifications Selection sheet. For example, suppose the Aspen Physical Property System cannot find the parameters for a particular submodel (equation) in the ASPENPCD databank. If the PURE10 databank contains parameters for another equation, the Aspen Physical Property System will use that equation (most likely the DIPPR equation) to calculate the property for that component.

If your calculation contains any temperature-dependent property parameters, (such as CPIGDP for DIPPR ideal gas heat capacity, entered on the Properties Parameters Pure Component form), the Aspen Physical Property System sets THRSWT element 7 to 1 for that component. This default setting might not always be correct. If you know the equation number, you should enter it directly on the

Properties Parameters Pure-Components form. For example, suppose you want to use the:

- DIPPR equation form of heat of vaporization (DHVLDP) for a component

- Aspen equations for the remaining temperature dependent properties

Set the fourth element of the THRSWT parameter to 106 (see the table Pure Component Temperature-Dependent Properties, above), and the 1-3 and 5-8 elements to 0. If you want to set the other temperature-dependent properties to use what is defined for that component in the databank, leave the element blank.

Many different equations are available for DIPPR to use for any property of a component, although it is usually limited to two or three. The following table lists the available DIPPR equations and the corresponding equation (submodel) number.

Available DIPPR Equations

Equation Number	Equation Form
100	$Y = A + BT + CT^2 + DT^3 + ET^4$
101	$Y = \exp[A + B/T + C\ln T + DT^E]$
102	$Y = (AT^B)/(1 + C/T + D/T^2)$
103	$Y = A + B\exp{-[C/T D]}$
104	$Y = A + B/T + C/T^3 + D/T^8 + E/T^9$
105	$Y = A/B^{(1+(1-T/C)^D)}$
106	$Y = A(1 - Tr)^{(B+CTr+DTr^2+ETr^3)}$
107	$Y = A + B[(C/T)/SINH(C/T)]^2 + D[(E/T)/COSH(E/T)]^2$
114	$Y = A^2/t + B - 2ACt - ADt^2 - (C^2t^3)/3 - (CDt^4)/2 - (D^2t^5)/5$
116	$Y = A + Bt^{0.35} + Ct^{(2/3)} + Dt + Et^{(4/3)}$

This chapter help describes the Aspen, DIPPR, BARIN, and IK-CAPE equations for each property. For descriptions of the the BARIN equations for heat capacity and enthalpy, see BARIN Equations for Gibbs Energy, Enthalpy, Entropy, and Heat Capacity, this chapter.

The PPDS equations are available only to the customers who have licensed the PPDS databank from NEL.

Thermodynamic Property Models

This section describes the available thermodynamic property models in the Aspen Physical Property System. The following table provides a list of available models, with corresponding Aspen Physical Property System model names. The table provides phase types for which the model can be used and information on use of the model for pure components and mixtures.

Aspen Physical Property System thermodynamic property models include classical thermodynamic property models, such as activity coefficient models and equations of state, as well as solids and electrolyte models. The models are grouped according to the type of property they describe.

Thermodynamic Property Models

Equation-of-State Models

Property Model	Model Name(s)	Phase(s)	Pure	Mixture
ASME Steam Tables	ESH2O0,ESH2O	V L	X	—
BWR-Lee-Starling	ESBWR0, ESCSTBWR	V L	X	X
Benedict-Webb-Rubin-Starling	ESBWRS, ESBWRS0	V L	X	X
Hayden-O'Connell	ESHOC0,ESHOC	V	X	X
HF equation-of-state	ESHF0, ESHF	V	X	X
Ideal Gas	ESIG	V	X	X
Lee-Kesler	ESLK	V L	—	X
Lee-Kesler-Plöcker	ESLKP0,ESLKP	V L	X	X
NBS/NRC Steam Tables	ESSTEAM0,ESSTEAM	V L	X	—
Nothnagel	ESNTH0,ESNTH	V	X	X
Peng-Robinson-Boston-Mathias	ESPR0, ESPR	V L	X	X
Peng-Robinson-Wong-Sandler	ESPRWS0,ESPRWS	V L	X	X
Peng-Robinson-MHV2	ESPRV20,ESPRV2	V L	X	X
Predictive SRK	ESRKSV10, ESRKSV1	V L	X	X
Redlich-Kwong	ESRK0, ESRK	V	X	X
Redlich-Kwong-Aspen	ESRKA0,ESRKA	V L	X	X
Redlich-Kwong-Soave-Boston-Mathias	ESRKS0,ESRKS	V L	X	X
Redlich-Kwong-Soave-Wong-Sandler	ESRKSWS0, ESRKSWS	V L	X	X
Redlich-Kwong-Soave-MHV2	ESRKSV20, ESRKSV2	V L	X	X
Schwartzentruber-Renon	ESRKU0,ESRKU	V L	X	X
Soave-Redlich-Kwong	ESSRK, ESSRK0	V L	X	X
Standard Peng-Robinson	ESPRSTD0,ESPRSTD	V L	X	X
Standard Redlich-Kwong-Soave	ESRKSTD0,ESRKSTD	V L	X	X
VPA/IK-CAPE equation-of-state	ESVPA0, ESVPA	V	X	X

Property Model	Model Name(s)	Phase(s)	Pure	Mixture
Peng-Robinson Alpha functions	—	V L	X	—
RK-Soave Alpha functions	—	V L	X	—
Huron-Vidal mixing rules	—	V L	—	X
MHV2 mixing rules	—	V L	—	X
PSRK mixing rules	—	V L	—	X
Wong-Sandler mixing rules	—	V L	—	X

Activity Coefficient Models

Property Model	Model Name	Phase(s)	Pure	Mixture
Bromley-Pitzer(Chien-Null)	GMPT2	L	—	X
Chien-Null	GMCHNULL	L	—	X
Constant Activity Coefficient	GMCONS	S	—	X
Electrolyte NRTL	GMELC	L L1 L2	—	X
Ideal Liquid	GMIDL	L	—	X
NRTL(Non-Random-Two-Liquid)	GMRENON	L L1 L2	—	X
Pitzer	GMPT1	L	—	X
Polynomial Activity Coefficient	GMPOLY	S	—	X
Redlich-Kister	GMREDKIS	L S	—	X
Scatchard-Hildebrand	GMXSH	L	—	X
Three-Suffix Margules	GMMARGUL	L S	—	X
UNIFAC	GMUFAC	L L1 L2	—	X
UNIFAC (Lyngby modified)	GMUFLBY	L L1 L2	—	X
UNIFAC (Dortmund modified)	GMUFDMD	L L1 L2	—	X
UNIQUAC	GMUQUAC	L L1 L2	—	X
van Laar	GMVLAAR	L	—	X
Wagner interaction parameter	GMWIP	S	—	X
Wilson	GMWILSON	L	—	X
Wilson model with liquid molar volume	GMWSNVOL	L	—	X

Vapor Pressure and Liquid Fugacity Models

Property Model	Model Name	Phase(s)	Pure	Mixture
Extended Antoine/Wagner	PL0XANT	L L1 L2	X	—
Chao-Seader	PHL0CS	L	X	—
Grayson-Streed	PHL0GS	L	X	—
Kent-Eisenberg	ESAMIN	L	—	X
Maxwell-Bonnell	PL0MXBN	L L1 L2	X	—

Heat of Vaporization Models

Property Model	Model Name	Phase(s)	Pure	Mixture
Watson / DIPPR / IK-CAPE	DHVLWTSN	L	X	—
Clausius-Clapeyron Equation	DHVLWTSN	L	X	—

Molar Volume and Density Models

Property Model	Model Name	Phase(s)	Pure	Mixture
API Liquid Volume	VL2API	L	—	X
Brelvi-O'Connell	VL1BROC	L	—	X
Clarke Aqueous Electrolyte Volume	VAQCLK	L	—	X
Costald Liquid Volume	VL0CTD,VL2CTD	L	X	X
Debije-Hückel Volume	VAQDH	L	—	X
Rackett / DIPPR / IK-CAPE Liquid Volume	VL0RKT,VL2RKT	L	X	—
Rackett Mixture Liquid Volume	VL2RKT	L	X	X
Modified Rackett	VL2MRK	L	X	X
Solids Volume Polynomial	VS0POLY	S	X	—

Heat Capacity Models

Property Model	Model Name	Phase(s)	Pure	Mixture
Aqueous Infinite Dilution Heat Capacity Polynomial	—	L	—	X
Criss-Cobble Aqueous Infinite Dilution Ionic Heat Capacity	—	L	—	X
DIPPR / IK-CAPE Liquid Heat Capacity	HL0DIP	L	X	—
Ideal Gas Heat Capacity / DIPPR	—	V	X	X
Solids Heat Capacity Polynomial	HS0POLY	S	X	—

Solubility Correlation Models

Property Model	Model Name	Phase(s)	Pure	Mixture
Henry's constant	HENRY1	L	—	X
Water solubility	—	L	—	X

Other Models

Property Model	Model Name	Phase(s)	Pure	Mixture
Cavett Liquid Enthalpy Departure	DHL0CVT, DHL2CVT	L	X	X
BARIN Equations for Gibbs Energy, Enthalpy, Entropy and Heat Capacity	—	S L V	X	—
Electrolyte NRTL Enthalpy	HAQELC, HMXELC	L	—	X
Electrolyte NRTL Gibbs Energy	GAQELC, GMXELC	L	—	X
Liquid Enthalpy from Liquid Heat Capacity Correlation	DHL0DIP	L	X	X
Enthalpies Based on Different Reference Status	DHL0HREF	L V	X	X

Phases: V = Vapor; L = Liquid; S = Solid

An X indicates applicable to Pure or Mixture

Equation-of-State Models

The Aspen Physical Property System has 20 built-in equation-of-state property models. This section describes the equation-of-state property models available.

Model	Type
ASME Steam Tables	Fundamental
BWR-Lee-Starling	Virial
Benedict-Webb-Rubin-Starling	Virial
Hayden-O'Connell	Virial and association
HF Equation-of-State	Ideal and association
Huron-Vidal mixing rules	Mixing rules
Ideal Gas	Ideal
Lee-Kesler	Virial
Lee-Kesler-Plöcker	Virial
MHV2 mixing rules	Mixing rules
NBS/NRC Steam Tables	Fundamental
Nothnagel	Ideal
Peng-Robinson Alpha functions	Alpha functions
Peng-Robinson-Boston-Mathias	Cubic
Peng-Robinson-MHV2	Cubic
Peng-Robinson-Wong-Sandler	Cubic
Predictive SRK	Cubic
PSRK mixing rules	Mixing rules
Redlich-Kwong	Cubic
Redlich-Kwong-Aspen	Cubic
Redlich-Kwong-Soave-Boston-Mathias	Cubic
Redlich-Kwong-Soave-MHV2	Cubic
Redlich-Kwong-Soave-Wong-Sandler	Cubic
RK-Soave Alpha functions	Alpha functions
Schwartzentruber-Renon	Cubic
Soave-Redlich-Kwong	Cubic
Standard Peng-Robinson	Cubic
Standard Redlich-Kwong-Soave	Cubic
VPA/IK-CAPE equation-of-state	Ideal and association
Wong-Sandler mixing rules	Mixing rules

ASME Steam Tables

The ASME steam tables (1967) are implemented like any other equation-of-state in the Aspen Physical Property System. The steam tables can calculate any thermodynamic property of water or steam and form the basis of the STEAM-TA property method. There are no parameter requirements. The ASME steam tables are less accurate than the NBS/NRC steam tables.

ASME Steam Tables, Thermodynamic and Transport Properties of Steam, (1967).

K. V. Moore, Aerojet Nuclear Company, prepared for the U.S. Atomic Energy Commision, ASTEM - A Collection of FORTRAN Subroutines to Evaluate the 1967 ASME equations of state for water/steam and derivatives of these equations.

BWR-Lee-Starling

The Benedict-Webb-Rubin-Lee-Starling equation-of-state is the basis of the BWR-LS property method. It is a generalization by Lee and Starling of the virial equation-of-state for pure fluids by Benedict, Webb and Rubin. The equation is used for non-polar components, and can manage hydrogen-containing systems.

General Form:

$$Z_m = Z_m^{(0)} + \gamma Z_m^{(1)}$$

Where:

$$Z_m^{(0)}, Z_m^{(1)} = fcn(T, T_c, V_m, V_{cm})$$

Mixing Rules:

$$V_{cm}^a = \sum_i \sum_j x_i x_j V_{cij}^{*,a}$$

$$V_{cm}^b T_c = \sum_i \sum_j x_i x_j T_{cij} V_{cij}^b$$

$$V_{cm}^b T_c = \sum_i \sum_j x_i x_j \gamma_{ij} V_{cij}^c$$

Where:

$$a = b = 4.5/3; c = 3.5/5$$

$$V_{cij} = (1 - \varepsilon_{ij})^3 (V_{ci}^* V_{cj}^*)^{1/2}$$

$$T_{cij} = (1 - n_{ij})(T_{ci} T_{cj})^{1/2}$$

$$\gamma_{\iota\varphi} = (\gamma_i - \gamma_j)^{1/2}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCBWR	T_{ci}	TC	X	5.0	2000.0	TEMPERATURE
VCBWR	V_{ci}^*	VC	X	0.001	3.5	MOLE-VOLUME
BWRGMA	γ_i	OMEGA	X	-0.5	3.0	—
BWRKV	ε_{ij}	0	X	-5.0	1.0	—
BWRKT	η_{ij}	0	X	-5.0	1.0	—

Binary interaction parameters BWRKV and BWRKT are available in the Aspen Physical Property System for a large number of components. (See *Physical Property Data, Chapter 1*).

References

M.R. Brulé, C.T. Lin, L.L. Lee, and K.E. Starling, AIChE J., Vol. 28, (1982) p. 616.

Brulé et al., Chem. Eng., (Nov., 1979) p. 155.

Watanasiri et al., AIChE J., Vol. 28, (1982) p. 626.

Benedict-Webb-Rubin-Starling

The Benedict-Webb-Rubin-Starling equation-of-state is the basis of the BWRS property method. It is a modification by Han and Starling of the virial equation-of-state for pure fluids by Benedict, Webb and Rubin. This equation-of-state can be used for hydrocarbon systems that include the common light gases, such as H_2S, CO_2 and N_2.

The form of the equation-of-state is:

$$P = \rho_m RT + (B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4})\rho_m^2 + (bRT - a - \frac{d}{T})\rho_m^3$$

$$+ \alpha(a + \frac{d}{T})\rho_m^6 + \frac{c\rho_m^3}{T^2}(1 + \gamma\rho_m^2)\exp(-\gamma\rho_m^2)$$

Where:

$$B_0 = \sum_i x_i B_{0i}$$

$$A_0 = \sum_i \sum_j x_i x_i A_{0i}^{\frac{1}{2}} A_{oj}^{\frac{1}{2}}(1 - k_{ij})$$

$$C_0 = \sum_i \sum_j x_i x_i C_{0i}^{\frac{1}{2}} C_{oj}^{\frac{1}{2}}(1 - k_{ij})^3$$

$$\gamma = \left[\sum_i x_i \gamma_i^{\frac{1}{2}}\right]^2$$

$$b = \left[\sum_i x_i b_i^{\frac{1}{3}}\right]^3$$

$$a = \left[\sum_i x_i a_i^{\frac{1}{3}}\right]^3$$

$$\alpha = \left[\sum_i x_i \, \alpha_i^{\frac{1}{3}} \right]^3$$

$$c = \left[\sum_i x_i \, c_i^{\frac{1}{3}} \right]^3$$

$$D_0 = \sum_i \sum_j x_i x_i \, D_{0i}^{\frac{1}{2}} D_{oj}^{\frac{1}{2}} (1 - k_{ij})^4$$

$$d = \left[\sum_i x_i \, d_i^{\frac{1}{3}} \right]^3$$

$$E_0 = \sum_i \sum_j x_i x_i \, E_{0i}^{\frac{1}{2}} E_{oj}^{\frac{1}{2}} (1 - k_{ij})^5$$

$$k_{ij} = k_{ji}$$

In the mixing rules given above, A_{0i}, B_{0i}, C_{0i}, D_{0i}, E_{0i}, a_i, b_i, c_i, d_i, α_i, γ_i are pure component constants which can be input by the user. If the values of these parameters are not given, the Aspen Physical Property System will calculate them using the critical temperature, the critical volume (or critical density), the acentric factor and generalized correlations given by Han and Starling.

For best results, the binary parameter k_{ij} must be regressed using phase-equilibrium data such as VLE data.

Parameter Name/ Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
BWRSTC	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
BWRSVC	V_{ci}	VC	x	0.001	3.5	MOLE-VOLUME
BWRSOM	ω_i	OMEGA	x	–0.5	2.0	–
BWRSA/1	B_{0i}	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	MOLE-VOLUME
BWRSA/2	A_{0i}	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	PRESSURE * MOLE-VOL^2
BWRSA/3	C_{0i}	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	PRESSURE * TEMPERATURE^2 * MOLE-VOLUME^2
BWRSA/4	γ_i	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	MOLE-VOLUME^2
BWRSA/5	b_i	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	MOLE-VOLUME^2
BWRSA/6	a_i	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	PRESSURE * MOLE-VOL^3
BWRSA/7	α_i	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	MOLE-VOLUME^3
BWRSA/8	c_i	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	PRESSURE * TEMPERATURE^2 * MOLE-VOLUME^3
BWRSA/9	D_{0i}	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	PRESSURE * TEMPERATURE^3 * MOLE-VOLUME^2
BWRSA/10	d_i	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	PRESSURE * TEMPERATURE * MOLE-VOLUME^3
BWRSA/11	E_{0i}	$fcn(\omega_i, V_{ci}, T_{ci})$	x	–	–	PRESSURE * TEMPERATURE^4 * MOLE-VOLUME^2

Constants Used with the correlations of Han and Starling

Parameter	Methane	Ethane	Propane	n-Butane
B_{0i}	0.723251	0.826059	0.964762	1.56588
A_{0i}	7520.29	13439.30	18634.70	32544.70
C_{0i}	2.71092×10^{8}	2.95195×10^{9}	7.96178×10^{9}	1.37436×10^{10}
D_{0i}	1.07737×10^{10}	2.57477×10^{11}	4.53708×10^{11}	3.33159×10^{11}
E_{0i}	3.01122×10^{10}	1.46819×10^{13}	2.56053×10^{13}	2.30902×10^{12}
b_i	0.925404	3.112060	5.462480	9.140660
a_i	2574.89	22404.50	40066.40	71181.80
d_i	47489.1	702189.0	1.50520×10^{7}	3.64238×10^{7}
α_i	0.468828	0.909681	2.014020	4.009850
c_i	4.37222×10^{8}	6.81826×10^{9}	2.74461×10^{10}	7.00044×10^{10}
γ_i	1.48640	2.99656	4.56182	7.54122

Parameter	n-Pentane	n-Hexane	n-Heptane	n-Octane
B_{0i}	2.44417	2.66233	3.60493	4.86965
A_{0i}	51108.20	45333.10	77826.90	81690.60
C_{0i}	2.23931×10^{10}	5.26067×10^{10}	6.15662×10^{10}	9.96546×10^{10}
D_{0i}	1.01769×10^{12}	5.52158×10^{12}	7.77123×10^{12}	7.90575×10^{12}
E_{0i}	3.90860×10^{13}	6.26433×10^{14}	6.36251×10^{12}	3.46419×10^{13}
b_i	16.607000	29.498300	27.441500	10.590700
a_i	162185.00	434517.00	359087.00	131646.00
d_i	3.88521×10^{7}	3.27460×10^{7}	8351150.0	1.85906×10^{8}
α_i	7.067020	9.702300	21.878200	34.512400
c_i	1.35286×10^{11}	3.18412×10^{11}	3.74876×10^{11}	6.42053×10^{11}
γ_i	11.85930	14.87200	24.76040	21.98880

References

M. Benedict, G. B. Webb, and L. C. Rubin, J. Chem. Phys., Vol. 8, (1940), p. 334.

M. S. Han, and K. E. Starling , "Thermo Data Refined for LPG. Part 14: Mixtures", Hydrocarbon Processing, Vol. 51, No. 5, (1972), p.129.

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

Hayden-O'Connell   The Hayden-O'Connell equation-of-state calculates thermodynamic properties for the vapor phase. It is used in property methods NRTL-HOC, UNIF-HOC, UNIQ-HOC, VANL-HOC, and WILS-HOC, and is recommended for nonpolar, polar, and associating compounds. Hayden-O'Connell incorporates the chemical theory of dimerization. This model accounts for strong association and solvation effects, including those found in systems containing organic acids, such as acetic acid. The equation-of-state is:

$$Z_m = 1 + \frac{B_p}{RT}$$

Where:

$$B = \sum_i \sum_j x_i x_j B_{ij}(T)$$

$$B_{ij} = (B_{free-nonpolar})_{ij} + (B_{free-polar})_{ij} + (B_{metastable})_{ij} + (B_{bound})_{ij} + (B_{chem})_{ij}$$

- For nonpolar, non-associating species:

  $B_{free-nonpolar} = f_1(\sigma_{np}, \varepsilon_{np}, \omega_{np}, T)$, with

  $\sigma_{np} = g_1(\omega_{np}, T_c, p_c)$

  $\varepsilon_{np} = g_2(\omega_{np}, T_c)$, where

  $\omega_{np} = f_2(r^{gyr})$

- For polar, associating species:

  $B_{free-nonpolar} = f_3(\sigma_{fp}, \varepsilon_{fp}, \omega_{np}, T)$, with

  $\sigma_{fp} = g_3(\sigma_{np}, \omega_{np}, \xi)$

  $\varepsilon_{fp} = g_4(\varepsilon_{np}, \omega_{np}, \xi)$, where

  $\xi = \gamma_5(\sigma_{np}, \varepsilon_{np}, \omega_{np}, p, T)$

- For chemically bonding species:

  $B_{metastable} + B_{bound} = f_4(\sigma_c, \varepsilon_c, p, T)$, and

  $B_{chem} = f_5(\sigma_c, \varepsilon_c, \eta, T)$

  $\sigma_c = g_3(\sigma_{np}, \omega_{np}, \xi)$

  $\varepsilon_c = g_6(\varepsilon_{np}, \omega_{np}, \xi, \eta)$

Cross-Interactions

The previous equations are valid for dimerization and cross-dimerization if these mixing rules are applied:

$$\varepsilon = 0.7(\varepsilon_i \, \varepsilon_j)^{1/2} + 0.6\left(\frac{1}{\varepsilon_i} + \frac{1}{\varepsilon_j}\right)$$

$$\sigma = (\sigma_i \sigma_j)^{1/2}$$

$$\varepsilon = 0.7(\varepsilon_i \, \varepsilon_j)^{1/2} + 0.6\left(\frac{1}{\varepsilon_i} + \frac{1}{\varepsilon_j}\right)$$

$$\sigma = (\sigma_i \sigma_j)^{1/2}$$

$$\omega_{np} = \frac{(\omega_{n,pi} + \omega_{n,pj})}{2}$$

$$\boldsymbol{p} = (\boldsymbol{p}_i \boldsymbol{p}_j)^{1/2}$$

$\eta = 0$ unless a special solvation contribution can be justified (for example, i and j are in the same class of compounds). Many η values are present in the Aspen Physical Property System.

Chemical Theory

When a compound with strong association $(\eta \geq 4.5)$ is present in a mixture, the entire mixture is treated according to the chemical theory of dimerization.

The chemical reaction for the general case of a mixture of dimerizing components i and j is:

$$K_{ij}$$

$$i + j = ij$$

Where i and j refer to the same component.

The equation-of-state becomes:

$$\frac{pV}{RT} = n^t\left(1 + \frac{Bp}{RT}\right) \quad \text{with} \quad B = \sum_{i=1}^{nc} \sum_{j=1}^{nc} y_{ij}(B_{free})_{ij}$$

In this case, molar volume is equal to:

$$\frac{V}{n^t}$$

This represents true total volume over the true number of species n^t. However, the reported molar volume is:

$$\frac{V}{n^a}$$

This represents the true total volume over the apparent number of species n^a. If dimerization does not occur, n^a is defined as the number of species. $\dfrac{V}{n^a}$ reflects the apparently lower molar volume of an associating gas mixture.

The chemical equilibrium constant for the dimerization reaction on pressure basis K_p, is related to the true mole fractions and fugacity coefficients:

$$\frac{y_{ij}}{y_i y_j} \frac{\varphi_{ij}}{\varphi_i \varphi_j} = K_{ij} p$$

Where:

y_i and y_j	$=$	True mole fractions of monomers
y_{ij}	$=$	True mole fraction of dimer
φ_i	$=$	True fugacity coefficient of component i
K_{ij}	$=$	Equilibrium constant for the dimerization of i and j, on a pressure basis
	$=$	$-(\mathrm{B_{bound}} + \mathrm{B_{metastable}} + \mathrm{B_{chem}})_{ij}(2-\delta_{ij})/\mathrm{RT}$
δ_{ij}	$=$	1 for $i=j$
	$=$	0 for $i \ne j$

Apparent mole fractions y_i^a are reported, but in the calculation real mole fractions y_i, y_j, and y_{ij} are used.

The heat of reaction due to each dimerization is calculated according to:

$$\Delta_r H_m = -T^2 \frac{\mathrm{d}(\Delta_r G_m)}{\mathrm{d}T} = RT^2 \frac{\mathrm{d}(\ln K_{ij})}{\mathrm{d}T}$$

The sum of the contributions of all dimerization reactions, corrected for the ratio of apparent and true number of moles is added to the molar enthalpy departure $H_m^v - H_m^{ig}$.

Parameter Name/ Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
PC	p_{ci}	—	—	10^5	10^8	PRESSURE
RGYR	r_i^{gyr}	—	—	10^{-11}	5×10^{-9}	LENGTH
MUP	p_i	—	—	0.0	5×10^{-24}	DIPOLEMOMENT
HOCETA	η	0.0	X	—	—	—

The binary parameters HOCETA for many component pairs are available in the Aspen Physical Property System. These parameters are retrieved automatically when you specify any of the following property methods: NRTL-HOC, UNIF-HOC, UNIQ-HOC, VANL-HOC, and WILS-HOC.

References

J.G. Hayden and J.P. O'Connell, "A Generalized Method for Predicting Second Virial Coefficients," *Ind. Eng. Chem., Process Des. Dev.*, Vol. 14,No. 3, (1974), pp. 209 – 216.

HF Equation-of-State

HF forms oligomers in the vapor phase. The non-ideality in the vapor phase is found in important deviations from ideality in all thermodynamic properties. The HF equation accounts for the vapor phase nonidealities. The model is based on chemical theory and assumes the formation of hexamers.

Species like HF that associate linearly behave as single species. For example, they have a vapor pressure curve, like pure components. The component on which a hypothetical unreacted system is based is often called the apparent (or parent) component. Apparent components react to the true species. Electrolyte Calculation, Chapter 5, discusses apparent and true species. Abbott and van Ness (1992) provide details and basic thermodynamics of reactive systems.

The temperature-dependent hexamerization equilibrium constant, can fit the experimentally determined association factors. The built-in functionality is:

$$^{10}\log K = C_0 + \frac{C_1}{T} + C_2 \ln T + C_3 T \tag{1}$$

The constants C_0 and C_1 are from Long et al. (1943), and C_2 and C_3 are set to 0. The correlation is valid between 270 and 330 K, and can be extrapolated to about 370 K (cf. sec. 4). Different sets of constants can be determined by experimental data regression.

Molar Volume Calculation

The non-ideality of HF is often expressed using the association factor, f, indicating the ratio of apparent number of species to the real number or species. Assuming the ideal gas law for all true species in terms of (p, V, T) behavior implies:

$$pV_m = \left(\frac{1}{f}\right)RT \qquad (2)$$

Where the true number of species is given by $\frac{1}{f}$. The association factor is easily determined from (p, V, T) experiments. For a critical evaluation of data refer to Vanderzee and Rodenburg (1970).

If only one reaction is assumed for a mixture of HF and its associated species, (refer to Long et al., 1943), then:

$$6HF \leftrightarrow (HF)_6 \qquad (3)$$
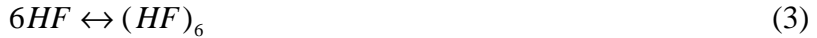
If p_1 represents the true partial pressure of the HF monomer, and p_6 represents the true partial pressure of the hexamer, then the equilibrium constant is defined as:

$$K = \frac{p_6}{(p_1)^6} \qquad (4)$$

The true total pressure is:

$$p = p_1 + p_6 \qquad (5)$$

If all hexamer were dissociated, the apparent total pressure would be the hypothetical pressure where:

$$p^a = p_1 + 6p_6 = p + 5p_6 \qquad (6)$$

When physical ideality is assumed, partial pressures and mole fractions are proportional. The total pressure in equation 5 represents the true number of species. The apparent total pressure from equation 6 represents the apparent number of species:

$$f = \frac{p^a}{p} = \frac{p_1 + 6p_6}{p_1 + p_6} = \frac{p + 5p_6}{p} = 1 + 5y_6 \qquad (7)$$

Note that the outcome of equation 7 is independent of the assumption of ideality. Equation 7 can be used to compute the number of true species $\frac{1}{f}$ for a mixture containing HF, but the association factor is defined differently.

If p_1 and p_6 are known, the molar volume or density of a vapor containing HF can be calculated using equations 2 and 7. The molar volume calculated is the true molar volume for 1 apparent mole of HF. This is because the volume of 1 mole of ideal gas (the true molar volume per true number of moles) is always equal to about 0.0224 m3/mol at 298.15 K.

True Mole Fraction (Partial Pressure) Calculation

If you assume the ideal gas law for a mixture containing HF, the apparent HF mole fraction is:

$$y^a = \frac{p_1^a}{p^a} = \frac{p_1 + 6p_6}{p + 5p_6} \tag{8}$$

The denominator of equation 8 is given by equation 6. The numerator (the apparent partial pressure of HF) is the hypothetical partial pressure only if all of the hexamer was dissociated. If you substitute equation 4, then equation 8 becomes:

$$y^a = \frac{p_1 + 6K(p_1)^6}{p + 5K(p_1)^6} \tag{9}$$

K is known from Long et al., or can be regressed from (p,V,T) data. The apparent mole fraction of HF, y^a, is known to the user and the simulator, but p_1, or $y = \frac{p_1}{p}$ must also be known in order to calculate the thermodynamic properties of the mixture. Equation 9 must be solved for. p_1

Equation 9 can be written as a polynomial in p_1 of degree 6:

$$K(6 - 5y^a)(p_1)^6 + p_1 - py^a = 0 \tag{9a}$$

A second order Newton-Raphson technique is used to determine p_1. Then p_6 can be calculated by equation 5, and f is known (equation 7).

Gibbs Energy and Fugacity

The apparent fugacity coefficient is related to the true fugacity coefficient and mole fractions:

$$\ln \varphi_i^a = \ln \varphi_i = \ln\left(\frac{y_1}{y^a}\right) \tag{10}$$

Equation 10 represents a correction to the ideal mixing term of the fugacity. The ratio of the true number of species to the apparent number of species is similar to the correction applied in equation 2.

Since the ideal gas law is assumed, the apparent fugacity coefficient is given by the equation. All variables on the right side are known.

$$\varphi_i^a = \frac{y_1}{y^a} = \frac{p_1}{py^a}$$ (11)

For pure HF, $y^a = 1$:

$$\ln \varphi_i^{*,a} = \ln y_1$$

From the fugacity coefficient, the Gibbs energy departure of the mixture or pure apparent components can be calculated:

$$G - G^{ig} = RT \sum_i \ln \varphi_i^a + RT \ln \frac{p}{p^{ref}}$$ (12)

$$\mu - \mu^{*,ig} = RT \ln \varphi_i^{*,a} + RT \ln \frac{p}{p^{ref}}$$ (12a)

Enthalpy and Entropy

For the enthalpy departure, the heat of reaction is considered. For an arbitrary gas phase reaction:

$$v_A A + v_B B = v_C C + v_D D$$ (13)

$$RT \ln K = RT \ln \frac{p_{C^c}^v p_{D^D}^v}{p_{A^A}^v p_{B^B}^v}$$ (14)

Where μ_i^* is the pure component thermodynamic potential or molar Gibbs energy of a component. Equation 4 represents the first two terms of the general equation 14. The second or third equality relates the equilibrium constant to the Gibbs energy of reaction, which is thus related to the enthalpy of reaction:

$$\Delta_r H_m = -T^2 \frac{d\Delta_r G_m}{dT} = RT^2 \frac{\partial(\ln K)}{\partial T}$$ (15)

All components are assumed to be ideal. The enthalpy departure is equal to the heat of reaction, per apparent number of moles:

$$H_m - H_m^{ig} = \frac{1}{f} \Delta_r H_m$$ (16)

$$H_{HF}^* - H_{HF}^{*,ig} = \frac{1}{f} \Delta_r H_m$$ (17)

From the Gibbs energy departure and enthalpy departure, the entropy departure can be calculated:

$$G_m = H_m - TS_m$$ (18)

Temperature derivatives for the thermodynamic properties can be obtained by straightforward differentiation.

Usage

The HF equation-of-state should only be used for vapor phase calculations. It is not suited for liquid phase calculations.

The HF equation-of-state can be used with any activity coefficient model for nonelectrolyte VLE. Using the Electrolyte NRTL model and the data package MHF2 is strongly recommended for aqueous mixtures (de Leeuw and Watanasiri, 1993).

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
ESHFK/1	C_0	43.65	—	—	—	—
ESHFK/2	C_1	-8910	—	—	—	—
ESHFK/3	C_2	0	—	—	—	—
ESHFK/4	C_3	0	—	—	—	—

M. M. Abbott and H. C. van Ness, "Thermodynamics of Solutions Containing Reactive Species, a Guide to Fundamentals and Applications," Fluid Phase Eq., Vol. 77, (1992) pp. 53 – 119.

V. V. De Leeuw and S. Watanasiri, "Modelling Phase Equilibria and Enthalpies of the System Water and Hydroflouric Acid Using an HF Equation-of-state in Conjunction with the Electrolyte NRTL Activity Coefficient Model," Paper presented at the 13th European Seminar on Applied Thermodynamics, June 9 – 12, Carry-le-Rouet, France, 1993.

R. W. Long, J. H. Hildebrand, and W. E. Morrell, "The Polymerization of Gaseous Hydrogen and Deuterium Flourides," J. Am. Chem. Soc., Vol. 65, (1943), pp. 182 – 187.

C. E. Vanderzee and W. WM. Rodenburg, "Gas Imperfections and Thermodynamic Excess Properties of Gaseous Hydrogen Flouride," J. Chem. Thermodynamics, Vol. 2, (1970), pp. 461 – 478.

Ideal Gas

The ideal gas law (ideal gas equation-of-state) combines the laws of Boyle and Gay-Lussac. It models a vapor as if it consisted of point masses without any interactions. The ideal gas law is used as a reference state for equation-of-state calculations, and can be used to model gas mixtures at low pressures (without specific gas phase interactions).

The equation is:

$$p = \frac{RT}{V_m}$$

Lee-Kesler   This equation-of-state model is based on the work of Lee and Kesler (1975). In this equation, the volumetric and thermodynamic properties of fluids based on the Curl and Pitzer approach (1958) have been analytically represented by a modified Benedict-Webb-Rubin equation-of-state (1940). The model calculates the molar volume, enthalpy departure, Gibbs free energy departure, and entropy departure of a mixture at a given temperature, pressure, and composition for either a vapor or a liquid phase. Partial derivatives of these quantities with respect to temperature can also be calculated.

Unlike the other equation-of-state models, this model does not calculate fugacity coefficients.

The compressibility factor and other derived thermodynamic functions of nonpolar and slightly polar fluids can be adequately represented, at constant reduced temperature and pressure, by a linear function of the acentric factor. In particular, the compressibility factor of a fluid whose acentric factor is ω, is given by the following equation:

$$Z = Z^{(0)} + \omega Z^{(1)}$$

Where:

$Z^{(0)}$ =   Compressibility factor of a simple fluid $(\omega = 0)$

$Z^{(1)}$ =   Deviation of the compressibility factor of the real fluid from $Z^{(0)}$

$Z^{(0)}$ and $Z^{(1)}$ are assumed universal functions of the reduced temperature and pressure.

Curl and Pitzer (1958) were quite successful in correlating thermodynamic and volumetric properties using the above approach. Their application employed tables of properties in terms of reduced temperature and pressure. A significant weakness of this method is that the various properties (for example, entropy departure and enthalpy departure) will not be exactly thermodynamically consistent with each other. Lee and Kesler (1975) overcame this drawback by an analytic representation of the tables with an equation-of-state. In addition, the range was extended by including new data.

In the Lee-Kesler implementation, the compressibility factor of any fluid has been written in terms of a simple fluid and a reference as follows:

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

In the above equation both $Z^{(0)}$ and $Z^{(1)}$ are represented as generalized equations of the BWR form in terms of reduced temperature and pressure. Thus,

$$Z^{(0)} = f^{(0)}(T/T_{c,} \, P/P_c)$$

$$Z^{(r)} = f^{(r)}(T/T_{c,} \, P/P_c)$$

Equations for the enthalpy departure, Gibbs free energy departure, and entropy departure are obtained from the compressibility factor using standard thermodynamic relationships, thus ensuring thermodynamic consistency.

In the case of mixtures, mixing rules (without any binary parameters) are used to obtain the mixture values of the critical temperature and pressure, and the acentric factor.

This equation has been found to provide a good description of the volumetric and thermodynamic properties of mixtures containing nonpolar and slightly polar components.

Symbol	Parameter Name	Default	Definition
T_c	TCLK	TC	Critical temperature
P_c	PCLK	PC	Critical pressure
ω	OMGLK	OMEGA	Acentric factor

B. I. Lee and M.G. Kesler, AIChEJ, Vol. 21, (1975), p. 510.

R. F. Curl and K.S. Pitzer, Ind. Eng. Chem., Vol. 50, (1958), p. 265.

M. Benedict, G. B. Webb, and L. C. Rubin, J. Chem. Phys., Vol. 8, (1940), p. 334.

Lee-Kesler-Plöcker The Lee-Kesler-Plöcker equation-of-state is the basis for the LK-PLOCK property method. This equation-of-state applies to hydrocarbon systems that include the common light gases, such as H_2S and CO_2. It can be used in gas-processing, refinery, and petrochemical applications.

The general form of the equation is:

$$Z_m = Z_m^o + \frac{\omega}{\omega^R}(Z_m^o - Z_m^R)$$

Where:

$$Z_m^o = f_o(T, T_c, V_m, V_{cm})$$

$$Z_m^R = f_R(T, T_c, V_m, V_{cm})$$

The f_o and f_R parameters are functions of the BWR form. The f_o parameter is for a simple fluid, and f_R is for reference fluid n-octane.

$$p_c = Z_{cm} R T_c / V_{cm}$$

The mixing rules are:

$$V_{cm} \quad = \quad \sum_i \sum_j x_i x_j V_{cij}$$

$$V_{cm}^{1/4} T_c \quad = \quad \sum_i \sum_j x_i x_j V_{cij}^{1/4} T_{cij}$$

$$\omega \quad = \quad \sum_i x_i \omega_i$$

$$Z_m \quad = \quad \sum_i x_i Z_{ci}$$

Where:

$$V_{cij} \quad = \quad \left[V_{ci}^{1/3} + V_{cj}^{1/3} \right]^{3/8}$$

$$T_{cij} \quad = \quad (1 + k_{ij})(T_{ci} T_{cj})^{1/2}$$

$$Z_{ci} \quad = \quad \begin{cases} 0.2905 - 0.085\omega_i & (Method\,1) \\ p_{ci}V_{ci}/RT_{ci} & (Method\,2) \end{cases}$$

$$k_{ij} \quad = \quad k_{ji}$$

The binary parameter k_{ij} is determined from phase-equilibrium data regression, such as VLE data. The Aspen Physical Property System stores the binary parameters for a large number of component pairs. These binary parameters are used automatically with the LK-PLOCK property method. If binary parameters for certain component pairs are not available, they can be estimated using built-in correlations. The correlations are designed for binary interactions among the components CO, CO_2, N_2, H_2, CH_4 alcohols and hydrocarbons. If a component is not CO, CO_2, N_2, H_2, CH_4 or an alcohol, it is assumed to be a hydrocarbon.

Parameter Name/ Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCLKP	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCLKP	p_{ci}	PC	x	10^5	10^8	PRESSURE
VCLKP	V_{ci}	VC	x	0.001	3.5	MOLE-VOLUME
OMGLKP	ω_I	OMEGA	x	-0.5	2.0	—
LKPZC	Z_{ci}	$fcn(\omega)$ (Method 1) $fcn(p_{ci}, V_{ci}, T_{ci})$ (Method 2)	x	0.1	0.5	—
LKPKIJ	k_{ij}	$fcn(T_{ci}V_{ci} / T_{cj}V_{cj})$	x	5.0	5.0	—

Method 1 is the default; Method 2 can be invoked by setting the value of LKPZC equal to zero.

Binary interaction parameters LKPKIJ are available for a large number of components in the Aspen Physical Property System.

References

B.I. Lee and M.G. Kesler, AIChE J., Vol. 21, (1975) p. 510; errata: AIChE J., Vol. 21, (1975) p. 1040.

V. Plöcker, H. Knapp, and J.M. Prausnitz, Ind. Eng. Chem., Process Des. Dev., Vol. 17, (1978), p. 324.

NBS/NRC Steam Tables   The NBS/NRC Steam Tables are implemented like any other equation-of-state in the Aspen Physical Property System. These steam tables can calculate any thermodynamic property of water. The tables form the basis of the STEAMNBS and STMNBS2 property methods. There are no parameter requirements. They are the most accurate steam tables in the Aspen Physical Property System. The STMNBS2 model uses the same equations as STEAMNBS but with different root search method. The STMNBS2 method is recommended for use with the SRK, BWRS, MXBONNEL and GRAYSON2 property methods.

References

L. Haar, J.S. Gallagher, and J.H. Kell, "NBS/NRC Steam Tables," (Washington: Hemisphere Publishing Corporation, 1984).

Nothnagel

The Nothnagel equation-of-state calculates thermodynamic properties for the vapor phase. It is used in property methods NRTL-NTH, UNIQ-NTH, VANL-NTH, and WILS-NTH. It is recommended for systems that exhibit strong vapor phase association. The model incorporates the chemical theory of dimerization to account for strong association and solvation effects, such as those found in organic acids, like acetic acid. The equation-of-state is:

$$p = \frac{RT}{V_m - b}$$

Where:

$$b = \sum_{i=1}^{nc} y_i b_i + \sum_{i=1}^{nc} \sum_{j=1}^{i} y_{ij} b_{ij}$$

$$b_{ij} = \frac{(b_i^{1/3} + b_j^{1/3})^3}{8}$$

nc = Number of components in the mixture

The chemical reaction for the general case of a mixture of dimerizing components *i* and *j* is:
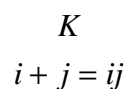
$$i + j \overset{K}{=} ij$$

The chemical equilibrium constant for the dimerization reaction on pressure basis K_p is related to the true mole fractions and fugacity coefficients:

$$\frac{y_{ij}}{y_i y_j} \frac{\varphi_{ij}}{\varphi_i \varphi_j} = K_{ij} p$$

Where:

y_i and y_j	=	True mole fractions of monomers
y_{ij}	=	True mole fraction of dimer
φ_i	=	True fugacity coefficient of component i
K_{ij}	=	Equilibrium constant for the dimerization of i and j, on a pressure basis

When accounting for chemical reactions, the number of true species n^t in the mixture changes. The true molar volume $\left(\frac{V}{n^t}\right)$ is calculated from the equation-of-state. Since both V and n^t change

in about the same proportion, this number does not change much. However, the reported molar volume is the total volume over the apparent number of species: $\dfrac{V}{n^a}$. Since the apparent number of species is constant and the total volume decreases with association, the quantity $\dfrac{V}{n^a}$ reflects the apparent contraction in an associating mixture.

The heat of reaction due to each dimerization can be calculated:

$$\Delta_r H_m = -T^2 \frac{d(\Delta_r G_m)}{dT} = RT^2 \frac{d(\ln K_{ij})}{dT}$$

The sum of the contributions of all dimerization reactions, corrected for the ratio of apparent and true number of moles, is added to the molar enthalpy departure:

$$(H_m^v - H_m^{ig})$$

The equilibrium constants can be computed using either built-in calculations or parameters you entered.

- Built-in correlations:

    $$\ln(RTK_{IJ}) = fcn(T, b_i, b_j, d_i, d_j, p_i, p_j)$$

    The pure component parameters b, d, and p are stored in the Aspen Physical Property System for many components.

Parameters you entered:

$$\ln K_{ii} = A_i + \frac{B_i}{T} + C_i \ln T + D_i T$$

In this method, you enter A_i B_i, C_i, and D_i on the Properties Parameters Unary.T-Dependent form. The units for K_{ii} is $pressure^{-1}$; use absolute units for temperature. If you enter K_{ii} and K_{jj}, then K_{jj} is computed from

$$K_{ij} = 2\sqrt{K_{ii}K_{jj}}$$

If you enter A_i B_i, C_i, and D_i, the equilibrium constants are computed using the parameters you entered. Otherwise the equilibrium constants are computed using built-in correlations.

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	5.0	2000.0	TEMPERATURE
TB	T_{bi}	—	4.0	2000.0	TEMPERATURE
PC	p_{ci}	—	10^5	10^8	PRESSURE
NTHA/1	b_i	$0.199 RT_{ci}/p_{ci}$	0.01	1.0	MOLE-VOLUME
NTHA/2	d_i	0.33	0.01	3.0	—
NTHA/3	p_i	0	0.0	1.0	—
NTHK/1	A_i	—	—	—	PRESSURE
NTHK/2	B_i	0	—	—	TEMPERATURE
NTHK/3	C_i	0	—	—	TEMPERATURE
NTHK/4	D_i	0	—	—	TEMPERATURE

References

K.-H. Nothnagel, D. S. Abrams, and J.M. Prausnitz, "Generalized Correlation for Fugacity Coefficients in Mixtures at Moderate Pressures," Ind. Eng. Chem., Process Des. Dev., Vol. 12, No. 1 (1973), pp. 25 – 35.

Peng-Robinson-Boston-Mathias

The Peng-Robinson-Boston-Mathias equation-of-state is the basis for the PR-BM property method. It is the Peng-Robinson equation-of-state with the Boston-Mathias alpha function (see Peng-Robinson Alpha Functions). It is recommended for hydrocarbon processing applications such as gas processing, refinery, and petrochemical processes. Its results are comparable to those of the Redlich-Kwong-Soave equation-of-state.

The equation for the BM model is:

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

Where:

$$b = \sum_i x_i b_i$$

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{ij})$$

$$b_i = fcn(T_{ci}, p_{ci})$$

$$a_i = fcn(T, T_{ci}, p_{ci}, \omega_i)$$

$$k_{ij} = k_{ji}$$

The parameter α_i is calculated by the standard Peng-Robinson formulation at supercritical temperatures. If the component is supercritical, the Boston-Mathias extrapolation is used (see Peng-Robinson Alpha Functions).

For best results, the binary parameter k_{ij} must be determined from phase equilibrium data regression, (for example, VLE data).

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCPR	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCPR	p_{ci}	PC	x	10^5	10^8	PRESSURE
OMGPR	ω_i	OMEGA	x	-0.5	2.0	—
PRKIJ	k_{ij}	0	x	-5.0	5.0	—

Binary interaction parameters PRKIJ are available for a large number of components in the Aspen Physical Property System.

References

D.-Y. Peng and D. B. Robinson, "A New Two-Constant Equation-of-state," Ind Eng. Chem. Fundam., Vol. 15, (1976), pp. 59–64.

Peng-Robinson-MHV2   This model uses the Peng-Robinson equation-of-state for pure compounds. The mixing rules are the predictive MHV2 rules. Several alpha functions can be used in the Peng-Robinson-MHV2 equation-of-state model. For a more accurate description of the pure component behavior. The pure component behavior and parameter requirements are described in Standard Peng-Robinson, or in Peng-Robinson Alpha Functions.

The MHV2 mixing rules are an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules. For more details, see MHV2 Mixing Rules., this chapter.

Predictive SRK (PSRK)   This model uses the Redlich-Kwong-Soave equation-of-state for pure compounds. The mixing rules are the predictive Holderbaum rules, or PSRK method. Several alpha functions can be used in the PSRK equation-of-state model. For a more accurate description of the pure component behavior. The pure component behavior and parameter requirements are described in Standard Redlich-Kwong-Soave and in Soave Alpha Functions.

The PSRK method is an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules. For more details, see Predictive Soave-Redlich-Kwong-Gmehling Mixing Rules., this chapter.

Peng-Robinson-Wong-Sandler	This model uses the Peng-Robinson equation-of-state for pure compounds. The mixing rules are the predictive Wong-Sandler rules. Several alpha functions can be used in the Peng-Robinson-Wong-Sandler equation-of-state model. For a more accurate description of the pure component behavior. The pure component behavior and parameter requirements are described in Peng-Robinson, and in Peng-Robinson Alpha Functions.

The Wong-Sandler mixing rules are an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules. For more details see Wong-Sandler Mixing Rules., this chapter.

Redlich-Kwong	The Redlich-Kwong equation-of-state can calculate vapor phase thermodynamic properties for the following property methods: NRTL-RK, UNIFAC, UNIF-LL, UNIQ-RK, VANL-RK, and WILS-RK. It is applicable for systems at low to moderate pressures (maximum pressure 10 atm) for which the vapor-phase nonideality is small. The Hayden-O'Connell model is recommended for a more nonideal vapor phase, such as in systems containing organic acids. It is not recommended for calculating liquid phase properties.

The equation for the model is:

$$p = \frac{RT}{V_m - b} - \frac{a/T^{0.5}}{V_m(V_m + b)}$$

Where:

$$\sqrt{a} = \sum_i x_i \sqrt{a_i}$$

$$b = \sum_i x_i b_i$$

$$a_i = \frac{0.42748023 R^2 T_{ci}^{1.5}}{p_{ci}}$$

$$b_i = \frac{0.08664035\, RT_{ci}}{p_{ci}}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	Tci	—	—	5.0	2000.0	TEMPERATURE
PC	pci	—	—	10^5	10^8	PRESSURE

References

O. Redlich and J.N.S. Kwong, "On the Thermodynamics of Solutions V. An Equation-of-state. Fugacities of Gaseous Solutions," Chem. Rev., Vol. 44, (1979), pp. 223 – 244.

Redlich-Kwong-Aspen
The Redlich-Kwong-Aspen equation-of-state is the basis for the RK-ASPEN property method. It can be used for hydrocarbon processing applications. It is also used for more polar components and mixtures of hydrocarbons, and for light gases at medium to high pressures.

The equation is the same as Redlich-Kwong-Soave:

$$p \quad = \quad \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)}$$

A quadratic mixing rule is maintained for:

$$a \quad = \quad \sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{a,ij})$$

An interaction parameter is introduced in the mixing rule for:

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

For ai an extra polar parameter is used:

$$a_i \quad = \quad fcn(T, T_{ci}, p_{ci}, \omega_i, \eta_i)$$

$$b_i \quad = \quad fcn(T_{ci}, p_{ci})$$

The interaction parameters are temperature-dependent:

$$k_{a,ij} \quad = \quad k_{a,ij}^0 + k_{a,ij}^1 \frac{T}{1000}$$

$$k_{b,ij} \quad = \quad k_{b,ij}^0 + k_{b,ij}^1 \frac{T}{1000}$$

For best results, binary parameters k_{ij} must be determined from phase-equilibrium data regression, such as VLE data.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCRKA	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCRKA	p_{ci}	PC	x	10^5	10^8	PRESSURE
OMGRKA	ω_i	OMEGA	x	-0.5	2.0	—
RKAPOL	η_i	0	x	-2.0	2.0	—
RKAKA0	$k_{a,ij}^0$	0	x	-5.0	5.0	—
RKAKA1	$k_{a,ij}^1$	0	x	-15.0	15.0	TEMPERATURE
RKAKB0	$k_{b,ij}^0$	0	x	-5.0	5.0	—
RKAKB1	$k_{b,ij}^1$	0	x	-15.0	15.0	TEMPERATURE

Absolute temperature units are assumed for RKAKA1 and RKAKB1.

References

Mathias, P.M., "A Versatile Phase Equilibrium Equation-of-state", Ind. Eng. Chem. Process Des. Dev., Vol. 22, (1983), pp. 385 – 391.

Redlich-Kwong-Soave-Boston-Mathias

The Redlich-Kwong-Soave-Boston-Mathias equation-of-state is the basis for the RKS-BM property method. It is the Redlich-Kwong-Soave equation-of-state with the Boston-Mathias alpha function (see Soave Alpha Functions). It is recommended for hydrocarbon processing applications, such as gas-processing, refinery, and petrochemical processes. Its results are comparable to those of the Peng-Robinson-Boston-Mathias equation-of-state.

The equation is:

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

Where:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{ij})$$

$$b = \sum_i x_i b_i$$

$$a_i = fcn(T, T_{ci}, p_{ci}, \omega_i)$$

$$b_i = fcn(T_{ci}, p_{ci})$$

$$k_{ij} = k_{ji}$$

The parameter a_i is calculated by the standard Soave formulation at supercritical temperatures. If the component is supercritical, the Boston-Mathias extrapolation is used (see Soave Alpha Functions).

For best results, binary parameters k_{ij} must be determined from phase-equilibrium data regression (for example, VLE data).

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCRKS	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCRKS	p_{ci}	PC	x	10^5	10^8	PRESSURE
OMGRKS	ω_i	OMEGA	x	-0.5	2.0	—
RKSKIJ	k_{ij}	0	x	-5.0	5.0	—

Binary interaction parameters RKSKIJ are available for a large number of components in the Aspen Physical Property System.

References

G. Soave, "Equilibrium Constants for Modified Redlich-Kwong Equation-of-state," Chem. Eng. Sci., Vol. 27, (1972), pp. 1196 – 1203.

Redlich-Kwong-Soave-Wong-Sandler

This equation-of-state model uses the Redlich-Kwong-Soave equation-of-state for pure compounds. The predictive Wong-Sandler mixing rules are used. Several alpha functions can be used in the Redlich-Kwong-Soave-Wong-Sandler equation-of-state model for a more accurate description of the pure component behavior. The pure component behavior and parameter requirements are described in Standard Redlich-Kwong-Soave, and in Soave Alpha Functions.

The Wong-Sandler mixing rules are an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules. For more details, see Wong-Sandler Mixing Rules., this chapter.

Redlich-Kwong-Soave-MHV2

This equation-of-state model uses the Redlich-Kwong-Soave equation-of-state for pure compounds. The predictive MHV2 mixing rules are used. Several alpha functions can be used in the RK-Soave-MHV2 equation-of-state model. For a more accurate description of the pure component behavior. The pure component behavior and its parameter requirements are described in Standard Redlich-Kwong-Soave, and in Soave Alpha Functions.

The MHV2 mixing rules are an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules. For more details, see MHV2 Mixing Rules., this chapter.

Schwartzentruber-Renon   The Schwartzentruber-Renon equation-of-state is the basis for the SR-POLAR property method. It can be used to model chemically nonideal systems with the same accuracy as activity coefficient property methods, such as the WILSON property method. This equation-of-state is recommended for highly non-ideal systems at high temperatures and pressures, such as in methanol synthesis and supercritical extraction applications.

The equation for the model is:

$$p = \frac{RT}{V_M + c - b} - \frac{a}{(V_m + c)(V_m + c + b)}$$

Where:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} [1 - k_{a,ij} - l_{ij}(x_i - x_j)]$$

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

$$c = \sum_i x_i c_i$$

$$a_i = fcn(T, T_{ci}, p_{ci}, \omega_i, q_{0i}, q_{1i}, q_{2i})$$

$$b_i = fcn(T_{ci}, p_{ci})$$

$$c_i = fcn\left(\frac{T}{T_{ci}}, c_{0i}, c_{1i}, c_{2i}\right)$$

$$k_{a,ij} = k_{a,ij}^0 + k_{a,ij}^1 T + k_{a,ij}^2 / T$$

$$l_{ij} = l_{ij}^0 + l_{ij}^1 T + l_{ij}^2 / T$$

$$k_{b,ij} = k_{b,ij}^0 + k_{b,ij}^1 T + k_{b,ij}^2 / T$$

$$k_{a,ij} = k_{a,ji}$$

$$l_{ij} = -l_{ji}$$

$$k_{b,ij} = k_{b,ji}$$

The binary parameters $k_{a,ij}$, $k_{b,ij}$, and l_{ij} are temperature-dependent. In most cases, $k_{a,ij}^0$ and l_{ij}^0 are sufficient to represent the system of interest.

VLE calculations are independent of c. However, c does influence the fugacity values and can be adjusted to (liquid) molar volumes.

For a wide temperature range, adjust c_{io} to the molar volume at 298.15K or at boiling temperature.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCRKU	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCRKU	p_{ci}	PC	x	105	108	PRESSURE
OMGRKU	ω_i	OMEGA	x	-0.5	2.0	—
RKUPP0	q_{0i}	—	x	—	—	—
RKUPP1	q_{1i}	0	x	—	—	—
RKUPP2	q_{2i}	0	x	—	—	—
RKUC0	c_{0i}	0	x	—	—	—
RKUC1	c_{1i}	0	x	—	—	—
RKUC2	c_{2i}	0	x	—	—	—
RKUKA0	$k_{a,ij}^{0}$	0	x	—	—	—
RKUKA1	$k_{a,ij}^{1}$	0	x	—	—	TEMPERATURE
RKUKA2	$k_{a,ij}^{2}$	0	x	—	—	TEMPERATURE
RKULA0	l_{ij}^{0}	0	x	—	—	—
RKULA1	l_{ij}^{1}	0	x	—	—	TEMPERATURE
RKULA2	l_{ij}^{2}	0	x	—	—	TEMPERATURE
RKUKB0	$k_{b,ij}^{0}$	0	x	—	—	—
RKUKB1	$k_{b,ij}^{1}$	0	x	—	—	TEMPERATURE
RKUKB2	$k_{b,ij}^{2}$	0	x	—	—	TEMPERATURE

For polar components (dipole moment $\gg 0$), if you do not enter q_{0i}, the system estimates q_{0i}, q_{1i}, q_{2i} from vapor pressures using the Antoine vapor pressure model.

If you do not enter at least one of the binary parameters $k_{a,ij}^{0}$, $k_{a,ij}^{2}$, l_{ij}^{0}, l_{ij}^{2}, $k_{b,ij}^{0}$, or $k_{b,ij}^{2}$ the system estimates $k_{a,ij}^{0}$, $k_{a,ij}^{2}$, l_{ij}^{0}, and l_{ij}^{2} from the UNIFAC model.

Absolute temperature units are assumed for RKUKA2, RKULA2, and RKUKB2.

References

G. Soave, "Equilibrium Constants for Modified Redlich-Kwong Equation-of-state," Chem. Eng. Sci., Vol. 27, (1972), pp. 1196 - 1203.

J. Schwartzentruber and H. Renon, "Extension of UNIFAC to High Pressures and Temperatures by the Use of a Cubic Equation-of-State," Ind. Eng. Chem. Res., Vol. 28, (1989), pp. 1049 – 1955.

A. Peneloux, E. Rauzy, and R. Freze, "A Consistent Correction For Redlich-Kwong-Soave Volumes", *Fluid Phase Eq.*, Vol. 8, (1982), pp. 7–23.

Soave-Redlich-Kwong   The Soave-Redlich-Kwong equation-of-state is the basis of the SRK property method. This model is based on the same equation of state as the Redlich-Kwong-Soave model. However, this model has several important differences.

- A volume translation concept introduced by Peneloux and Rauzy is used to improve molar liquid volume calculated from the cubic equation of state.

- Improvement in phase equilibrium calculations for mixtures containing water and hydrocarbons is achieved by using the Kabadi-Danner modification for the mixing rules.

- Improvement in enthalpy of water is achieved by using the NBS Steam Table

- Improvement in speed of computation for equation based calculation is achieved by using composition independent fugacity.

This equation-of-state can be used for hydrocarbon systems that include the common light gases, such as H_2S, CO_2 and N_2.

The form of the equation-of-state is:

$$p = \frac{RT}{V_m + c - b} - \frac{a}{(V_m + c)(V_m + c + b)}$$

Where:

$$a = \sum_i \sum_j x_i x_i a_{ij} + \sum_i a''_{wi} x_w^2 x_i$$

$$a_{ij} = a_{ji} \; ; \; a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij})$$

$$k_{ij} = a_{ij} + b_{ij}T \;\; ; \;\;\;\; k_{ij} = k_{ji}$$

If the Kabadi – Danner option is used, then $a_{ij} = a'_{wj}$, where i is water and j is a hydrocarbon.

$$a'_{wj} = (a_w a_j)^{1/2}(1 - k_{wj})$$

The best values of k_{wj} were obtained from experimental data. Results are given for seven homologous series(see table 1).

The term $\sum_i a''_{wi} x_w^2 x_i$ is used only when the Kabadi – Danner option is enabled, where:

$$a''_{wi} = G_i \left[1 - \left(\frac{T}{T_{cw}} \right)^{0.80} \right]$$

G_i is the sum of the group contributions of different groups which make up a molecule of hydrocarbon i.

$$G_i = \sum g_l$$

g_l is the group contribution parameter for groups constituting hydrocarbons(see table 2).

$$b = \sum_i x_i b_i$$

$$c = \sum_i x_i c_i$$

$$a_i = f(T, T_{ci}, P_{ci}, \omega_i)$$

$$b_i = f(T, T_{ci}, P_{ci})$$

$$c_i = 0.40768 \left(\frac{RT_{ci}}{P_{ci}} \right) (0.29441 - z_{RAi})$$

For best results, the binary parameter k_{ij} must be regressed using phase-equilibrium data such as VLE.

This model is very flexible and has many options that you can select as described in the following table:

Option Code	Value	Description
1	0	Standard SRK alpha function for Tr < 1, Boston-Mathias alpha function for Tr > 1
	1	Standard SRK alpha function for all
	2	Grabovsky – Daubert alpha function for H2 and standard SRK alpha function for others (default)
2	0	Standard SRK mixing rules (default)
	1	Kabadi – Danner mixing rules
3	0	Do not calculate enthalpy of water from steam table
	1	Calculate enthalpy of water from steam table (default)
4	0	Do not apply the Peneloux liquid volume correction
	1	Apply the liquid volume correction (default)
5	0	Use analytical method for root finding (default)
	2	Use numerical method for root finding

Best Fit Values of k_{wj} **for Different Homologous Series with Water**

Homologous series	k_{wj}
Alkanes	0.500
Alkenes	0.393
Dialkenes	0.311
Acetylenes	0.348
Naphthenes	0.445
Cycloalkenes	0.355
Aromatics	0.315

Group Constituting Hydrocarbons and Their Group Contribution Parameters

Group I	g_l, atm m$^6 \times 10^5$
CH4	1.3580
– CH3	0.9822
– CH2 –	1.0780
> CH –	0.9728
> C <	0.8687
– CH2 – (cyclic)	0.7488
> CH – (cyclic)	0.7352
– CH = CH – (cyclic) †	0.6180
CH2 = CH2	1.7940
CH2 = CH –	1.3450
CH2 = C<	0.9066
CH $\equiv$ CH	1.6870
CH $\equiv$ C –	1.1811
– CH =	0.5117
> C = (aromatic)	0.3902

† This value is obtained from very little data. Might not be reliable.

Parameter Name/ Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
SRKTC	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
SRKPC	p_{ci}	PC	x	10^5	10^8	PRESSURE
SRKOMG	ω_i	OMEGA	x	–0.5	2.0	—
SRKWF	G_i	0	x	—	—	—
SRKWK	k_{wi}	0	x	—	—	—
SRKZRA	z_{RA}	RKTZRA	x	—	—	—
SRKAIJ	a_{ij}	0	x	—	—	—
SRKBIJ	b_{ij}	0	x	—	—	TEMPERATURE

References

G. Soave, "Equilibrium Constants for Modified Redlich-Kwong Equation-of-state," Chem. Eng. Sci., Vol. 27, (1972), pp. 1196 - 1203.

A. Peneloux, E. Rauzy, and R. Freze, "A Consistent Correction For Redlich-Kwong-Soave Volumes", Fluid Phase Eq., Vol. 8, (1982), pp. 7–23.

V. Kabadi, and R. P. Danner, "A Modified Soave-Redlich-Kwong Equation of State for Water-Hydrocarbon Phase Equilibria", Ind. Eng. Chem. Process Des. Dev., Vol. 24, No. 3, (1985), pp. 537-541.

Standard Peng-Robinson The Standard Peng-Robinson equation-of-state is the basis for the PENG-ROB property method. It is the Peng-Robinson equation-of-state with the Boston-Mathias alpha function (see Peng-Robinson Alpha Functions). It is recommended for hydrocarbon processing applications such as gas processing, refinery, and petrochemical processes. Its results are comparable to those of the Standard Redlich-Kwong-Soave equation-of-state.

The equation for the BM model is:

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

Where:

$$b \quad = \quad \sum_i x_i b_i$$

$$a \quad = \quad \sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{ij})$$

$$b_i \quad = \quad fcn(T_{ci}, p_{ci})$$

$$a_i \quad = \quad fcn(T, T_{ci}, p_{ci}, \omega_i)$$

$$k_{ij} \quad = \quad k_{ji}$$

The parameter a_i is calculated according to the standard Peng-Robinson formulation (see Peng-Robinson Alpha Functions, equations 1 through 5).

For best results, the binary parameter k_{ij} must be determined from phase equilibrium data regression, (for example, VLE data). The Aspen Physical Property System also has built-in k_{ij} for a large number of component pairs. These parameters are used automatically with the PENG-ROB property method.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCPRS	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCPRS	p_{ci}	PC	x	10^5	10^8	PRESSURE
OMGPRKSS	ω_i	OMEGA	x	-0.5	2.0	—
PRKIJ	k_{ij}	0	x	-5.0	5.0	—

References

D.-Y. Peng and D. B. Robinson, "A New Two-Constant Equation-of-state," Ind. Eng. Chem. Fundam., Vol. 15, (1976), pp. 59–64.

Standard Redlich-Kwong-Soave

The Standard Redlich-Kwong-Soave-Boston-Mathias equation-of-state is the basis for the RK-SOAVE property method. It is recommended for hydrocarbon processing applications, such as gas-processing, refinery, and petrochemical processes. Its results are comparable to those of the Peng-Robinson equation-of-state.

The equation is:

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

Where:

$$a \quad = \quad \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})$$

$$b \quad = \quad \sum_i x_i b_i$$

$$a_i \quad = \quad fcn(T, T_{ci}, p_{ci}, \omega_i)$$

$$b_i \quad = \quad fcn(T_{ci}, p_{ci})$$

$$k_{ij} = k_{ji}$$

The parameter a_i is calculated according to the standard Soave formulation (see Soave Alpha Functions, equations 1, 2, 3, 5, and 6).

For best results, binary parameters k_{ij} must be determined from phase-equilibrium data regression (for example, VLE data). The Aspen Physical Property System also has built-in k_{ij} for a large number of component pairs. These binary parameters are used automatically with the RK-SOAVE property method.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCRKSS	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCRKSS	p_{ci}	PC	x	10^5	10^8	PRESSURE
OMRKSS	ω_i	OMEGA	x	-0.5	2.0	—
RKSKIJ	k_{ij}	0	x	-5.0	5.0	—

Binary interaction parameters RKSKIJ are available for a large number of components in the Aspen Physical Property System.

References

G. Soave, "Equilibrium Constants for Modified Redlich-Kwong Equation-of-state," Chem. Eng. Sci., Vol. 27, (1972), pp. 1196 – 1203.

J. Schwartzentruber and H. Renon, "Extension of UNIFAC to High Pressures and Temperatures by the Use of a Cubic Equation-of-state," Ind. Eng. Chem. Res., Vol. 28, (1989), pp. 1049 – 1955.

A. Peneloux, E. Rauzy, and R. Freze, "A Consistent Correction For Redlich-Kwong-Soave Volumes", Fluid Phase Eq., Vol. 8, (1982), pp. 7–23.

VPA/IK-CAPE Equation-of-State

The VPA/IK-CAPE equation of state is similar to the HF equation of state but allows dimerization, tetramerization and hexamerization to occur simultaneously. 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)

To get the largest possible flexibility of the model all these kinds of association can occur simultaneously, for example, in a mixture containing acetic acid and HF. Up to five components can associate, and any number of inert components are allowed. This is the only difference between this model and the HF equation of state, which account only the hexamerization of HF.

Symbols

In the following description, these symbols are used:

y_i = Apparent concentration

z_{in} = True concentration, for component i and degree of association $n=1, 2, 4, 6$

$$z_{i2} = z_{i4} = z_{i6} = 0 \text{ for } i > 5$$

z_{Mij} = True concentration of cross-dimers of components i and j, for i,j 1 to 5.

p_0 = Reference pressure

k = Number of components

Association Equilibria

Every association equilibrium reaction

$$n \cdot (i) \leftrightarrow (i)_n \tag{1}$$

$$(i) + (j) \leftrightarrow (ij) \tag{2}$$

is described by the equilibrium constants

$$K_{in} = \frac{z_{in}}{z_{i1}^n (p/p_0)^{n-1}} \tag{3}$$

$$K_{Mij} = \frac{z_{Mij}}{z_{i1} z_{j1} (p/p_0)} \tag{4}$$

By setting

$$\ln K_{in} = A_{in} + \frac{B_{in}}{T} \tag{5}$$

$$K_{Mij} = 2\sqrt{K_{i2} K_{j2}} \tag{6}$$

their temperature dependence can be reproduced.

To evaluate the true concentration of every complex z_{in}, the following nonlinear systems of equations are to be solved:

Total mass balance:
The sum of true concentrations is unity.

$$\sum_i \sum_n z_{in} + \sum_i \sum_{j>i} z_{Mij} = 1$$

$$\sum_i \sum_n K_{in} z_{i1}^n (p/p_0)^{n-1} + \sum_i \sum_{j>i} K_{Mij} z_{i1} z_{j1} (p/p_0) = 1 \qquad (7)$$

Mass balance for every component i>1:
The ratio of the monomers of each component i>1 and component i=1 occurring in the various complexes must be equal to the ratio of their apparent concentrations.

$$\frac{\displaystyle\sum_n nz_{in} + \sum_{j \neq i} z_{Mij}}{\displaystyle\sum_n nz_{1n} + \sum_{j \neq 1} z_{M1j}} = \frac{y_i}{y_1}$$

$$\frac{\displaystyle\sum_n nK_{in} z_{i1}^n (p/p_0)^{n-1} + \sum_{j \neq i, j \leq 5} K_{Mij} z_{i1} z_{j1} (p/p_0)}{\displaystyle\sum_n nK_{1n} z_{11}^n (p/p_0)^{n-1} + \sum_{j \neq 1, j \leq 5} K_{M1j} z_{11} z_{j1} (p/p_0)} = \frac{y_i}{y_1} \qquad (8)$$

Thus, a system of k nonlinear equations for k unknowns z_{i1} has

been developed. After having solved it, all the z_{in} and z_{Mij} can be determined using equations (3, 4). This is the main step to evaluate all the properties needed for a calculation.

Specific Volume of the Gas Phase

The compressibility factor is defined by the ratio between the number of complexes and the number of monomers in the complexes.

$$v = \frac{RT}{P} \frac{\displaystyle\sum_i \sum_n z_{in} + \sum_i \sum_{j>i} z_{Mij}}{\displaystyle\sum_i \sum_n nz_{in} + 2\sum_i \sum_{j>i} z_{Mij}}$$

$$= \frac{RT}{P} \frac{1}{\displaystyle\sum_i \sum_n nz_{in} + 2\sum_i \sum_{j>i} z_{Mij}} \qquad (9)$$

The compressibility factor itself is

$$Z = \frac{1}{\displaystyle\sum_i \sum_n nz_{in} + 2\sum_i \sum_{j>i} z_{Mij}} \qquad (10)$$

Fugacity Coefficient

As is well-known from thermodynamics, the fugacity coefficient can be calculated by

$$\varphi_i = \frac{z_{i1}}{y_i} \tag{11}$$

Isothermal Enthalpy Departure

According to the ASPEN enthalpy model, an equation of state must supply an expression to compute the isothermal molar enthalpy departure between zero pressure and actual pressure. In the following section this enthalpy contribution per mole monomers is abbreviated by Δh_a.

Taking this sort of gas phase non-ideality into account, the specific enthalpy per mole can be written as

$$h_v = \sum_i y_i h_i^v + \Delta h_a \tag{12}$$

with

$$h_i^v = h_i^0 + \int_{T_o}^{T} c_{pi}^{i.g.} \, dT \tag{13}$$

to evaluate Δh_a, a mixture consisting of N monomers integrated in the complexes is considered. The quota of monomers i being integrated in a complex of degree n is given by

$$\frac{N_{in}}{N} = \frac{n z_{in}}{\sum_i \sum_n n z_{in} + 2 \sum_i \sum_{j>i} z_{Mij}} \tag{14}$$

and

$$\frac{N_{Mij}}{N} = \frac{2 z_{Mij}}{\sum_i \sum_n n z_{in} + 2 \sum_i \sum_{j>i} z_{Mij}} \tag{16}$$

respectively. For the reactions mentioned above:

$$n \cdot (i) \leftrightarrow (i)_n \tag{1}$$

$$(i) + (j) \leftrightarrow (ij) \tag{2}$$

the enthalpies of reaction are

$$\Delta h_{in} = -RB_{in} \tag{17}$$

$$\Delta h_{Mij} = -\frac{R}{2}(B_{i2} + B_{j2}) \tag{18}$$

as the van't Hoff equation

$$\Delta h = RT^2 \left(\frac{\partial \ln K}{\partial T} \right) \tag{19}$$

holds for this case.

For each monomer being integrated in a complex of degree n, its contribution to the enthalpy departure is $\Delta h_{in}/n$ or $\Delta h_{Mij}/2$, respectively. Hence, Δh_a can easily be derived by

$$\Delta h_a = \frac{\displaystyle\sum_i \sum_n N_{in}\Delta h_{in}/n + \sum_i \sum_{j>i} N_{Mij}\Delta h_{Mij}/2}{N}$$

$$\Delta h_a = \frac{\displaystyle\sum_i \sum_{n\neq 1} z_{in}\Delta h_{in} + \sum_i \sum_{j>i} z_{Mij}\Delta h_{Mij}}{\displaystyle\sum_i \sum_n nz_{in} + 2\sum_i \sum_{j>i} z_{Mij}} \tag{20}$$

Isothermal entropy and Gibbs energy departure:

A similar expression for Δg_a should hold as it does for the enthalpy departure (eq. 20):

$$\Delta g_a = \frac{\displaystyle\sum_i \sum_{n\neq 1} z_{in}\Delta g_{in} + \sum_i \sum_{j>i} z_{Mij}\Delta g_{Mij}}{\displaystyle\sum_i \sum_n nz_{in} + 2\sum_i \sum_{j>i} z_{Mij}} \tag{21}$$

using

$$\Delta g_{in} = -RT \ln K_{in} \tag{22}$$

and

$$\Delta g_{Mij} = -RT \ln K_{Mij} \tag{23}$$

$$\Delta s_{mix}^{id} = -R \sum_i y_i \ln y_i \tag{24}$$

Using the association model, more different species occur than can be distinguished. Thus, the equivalent expression for the entropy of mixing should be written with the true concentrations. As eq. 24 refers to 1 mole monomers, the expression should be weighted by the compressibility factor representing the true number of moles. The new expression is

$$\Delta s_{mix}^a = -RZ\left(\sum_i \sum_n z_{in} \ln z_{in} + \sum_i \sum_{j>i} z_{Mij} \ln z_{Mij}\right) \tag{25}$$

For Δg_a we obtain

$$\Delta g_a = \Delta h_a - T(\Delta s_{mix}^a - \Delta s_{mix}^{id}) \tag{26}$$

and, analogously,

$$\Delta s_a = \frac{\Delta h_a - \Delta g_a}{T} \tag{27}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
DMER/1	A_{i2}	0	X	–	–	–
DMER/2	B_{i2}	0	X	–	–	TEMPERATURE
TMER/1	A_{i4}	0	X	–	–	–
TMER/2	B_{i4}	0	X	–	–	TEMPERATURE
HMER/1	A_{i6}	0	X	–	–	–
HMER/2	B_{i6}	0	X	–	–	TEMPERATURE

References

M. M. Abbott and H. C. van Ness, "Thermodynamics of Solutions Containing Reactive Species, a Guide to Fundamentals and Applications," Fluid Phase Eq., Vol. 77, (1992) pp. 53–119.

V. V. De Leeuw and S. Watanasiri, "Modeling Phase Equilibria and Enthalpies of the System Water and Hydrofluoric Acid Using an HF Equation-of-state in Conjunction with the Electrolyte NRTL Activity Coefficient Model," Paper Presented at the 13th European Seminar on Applied Thermodynamics, June 9–12, Carry-le-Rouet, France, 1993.

R. W. Long, J. H. Hildebrand, and W. E. Morrell, "The Polymerization of Gaseous Hydrogen and Deuterium Fluorides," J. Am. Chem. Soc., Vol. 65, (1943), pp. 182–187.

C. E. Vanderzee and W. Wm. Rodenburg, "Gas Imperfections and Thermodynamic Excess Properties of Gaseous Hydrogen Fluoride," J. Chem. Thermodynamics, Vol. 2, (1970), pp. 461–478.

Peng-Robinson Alpha Functions

The pure component parameters for the Peng-Robinson equation-of-state are calculated as follows:

$$a_i = \alpha_i 0.45724 \frac{R^2 T_{ci}^2}{p_{ci}} \tag{1}$$

$$b_i = 0.07780 \frac{R T_{ci}}{p_{ci}} \tag{2}$$

These expressions are derived by applying the critical constraints to the equation-of-state under these conditions:

$$\alpha_i(T_{ci}) = 1.0 \tag{3}$$

The parameter α is a temperature function. It was originally introduced by Soave in the Redlich-Kwong equation-of-state. This parameter improves the correlation of the pure component vapor pressure. This approach was also adopted by Peng and Robinson:

$$\alpha_i(T) = [1 + m_i(1 - T_{ri}^{\frac{1}{2}})]^2 \tag{4}$$

Equation 3 is still represented. The parameter m_i can be correlated with the acentric factor:

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \tag{5}$$

Equations 1 through 5 are the standard Peng-Robinson formulation.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCPR	T_{ci}	TC	X	5.0	2000.0	TEMPERATURE
PCPR	p_{ci}	PC	X	10^5	10^8	PRESSURE
OMGPR	ω_i	OMEGA	X	-0.5	2.0	—

Boston-Mathias Extrapolation

For light gases at high reduced temperatures (> 5), equation 4 gives unrealistic results. The boundary conditions are that attraction between molecules should vanish for extremely high temperatures, and α reduces asymptotically to zero. Boston and Mathias derived an alternative function for temperatures higher than critical:

$$\alpha_i(T) = [\exp[c_i(1 - T_{ri}^{d_i})]]^2 \tag{6}$$

With

$$d_i = 1 + \frac{m_i}{2}$$

$$c_i = 1 - \frac{1}{d_i}$$

Where m_i is computed by equation 5, and equation 4 is used for subcritical temperatures. Additional parameters are not needed.

Mathias-Copeman Alpha Function

m_i is a constant for each component in equation 4. For very high accuracy or strongly curved vapor pressure behavior as a function of temperature, the Mathias-Copeman function is highly flexible

$$\alpha_{i(T)} = [1 + c_{1,i}(1 - T_{ri}^{\frac{1}{2}}) + c_{2,i}(1 - T_{ri}^{\frac{1}{2}})^2 + c_{3,i}(1 - T_{ri}^{\frac{1}{2}})^3]^2 \qquad (7)$$

For $c_{2,i} = 0$ and this expression reduces to the standard Peng-Robinson formulation if $c_{1,i} = m_i$. You can use vapor pressure data if the temperature is subcritical to regress the constants. If the temperature is supercritical, $c_{2,i}$ and $c_{3,i}$ are set to 0.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCPR	T_{ci}	TC	X	5.0	2000.0	TEMPERATURE
PCPR	p_{ci}	PC	X	10^5	10^8	PRESSURE
PRMCP/1	$c_{1,i}$	—	X	—	—	—
PRMCP/2	$c_{2,i}$	0	X	—	—	—
PRMCP/3	$c_{3,i}$	0	X	—	—	—

Schwartzentruber-Renon-Watanasiri Alpha Function

This method combines the flexibility of the Mathias-Copeman approach and the correction for highly reduced temperatures by Boston and Mathias:

$$\alpha_i(T) = [1 + m_i(1 - T_{ri}^{\frac{1}{2}}) - (1 - T_{ri}^{\frac{1}{2}})(p_{1,i} + p_{2,i}T_{ri} + p_{3,1}T_{ri}^2)]^2 \quad (8)$$

Where m_i is computed by equation 5. The polar parameters $p_{1,i}$, $p_{2,i}$ and $p_{3,i}$ are comparable with the c parameters of the Mathias-Copeman expression. Equation 8 reduces to the standard Peng-Robinson formulation if the polar parameters are zero. You can use vapor pressure data to regress the constants if the temperature is subcritical. Equation 8 is used only for below-critical temperatures. For above-critical temperatures, the Boston-Mathias extrapolation is used. Use equation 6 with:

$$d_i = 1 + \frac{1}{2}m_i - (p_{1,i} + p_{2,i} + p_{3,i}) \qquad (9)$$

$$c_i = 1 - \frac{1}{d_i}$$

(10)

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCPR	T_{ci}	TC	X	5.0	2000.0	TEMPERATURE
PCPR	p_{ci}	PC	X	10^5	10^8	PRESSURE
OMGPR	ω_i	OMEGA	X	-0.5	2.0	—
PRSRP/1	$p_{1,i}$	—	X	—	—	—
PRSRP/2	$p_{2,i}$	0	X	—	—	—
PRSRP/3	$p_{3,i}$	0	X	—	—	—

Use of Alpha Functions

The alpha functions in Peng-Robinson-based equation-of-state models is provided in the following table. You can verify and change the value of possible option codes on the Properties Property Method Model form.

Alpha function	Model name	First Option code
Standard Peng Robinson	ESPRSTD0, ESPRSTD	—
Standard PR/Boston-Mathias	ESPR0, ESPR	—
	ESPRWS0, ESPRWS	1
	ESPRV20, ESPRV2	1
Mathias-Copeman	ESPRWS0, ESPRWS	2
	ESPRV20, ESPRV2	2
Schwartzentruber-Renon-Watanasiri	ESPRWS0, ESPRWS	3 (default)
	ESPRV20, ESPRV2	3 (default)

References

J. F. Boston and P.M. Mathias, "Phase Equilibria in a Third-Generation Process Simulator" in Proceedings of the 2nd International Conference on Phase Equilibria and Fluid Properties in the Chemical Process Industries, West Berlin, (17-21 March 1980) pp. 823-849.

D.-Y. Peng and D.B. Robinson, "A New Two-Constant Equation-of-state," Ind. Eng. Chem. Fundam., Vol. 15, (1976), pp. 59-64.

P.M. Mathias and T.W. Copeman, "Extension of the Peng-Robinson Equation-of-state To Complex Mixtures: Evaluation of the Various Forms of the Local Composition Concept",Fluid Phase Eq., Vol. 13, (1983), p. 91.

J. Schwartzentruber, H. Renon, and S. Watanasiri, "K-values for Non-Ideal Systems:An Easier Way," Chem. Eng., March 1990, pp. 118-124.

G. Soave, "Equilibrium Constants for a Modified Redlich-Kwong Equation-of-state," Chem Eng. Sci., Vol. 27, (1972), pp. 1196-1203.

Soave Alpha Functions The pure component parameters for the Redlich-Kwong equation-of-state are calculated as:

$$a_i = \alpha_i 0.42747 \frac{R^2 T_{ci}^2}{p_{ci}} \tag{1}$$

$$b_i = 0.08664 \frac{RT_{ci}}{p_{ci}} \tag{2}$$

These expressions are derived by applying the critical constraint to the equation-of-state under these conditions:

$$\alpha_i(T_{ci}) = 1.0 \tag{3}$$

In the Redlich-Kwong equation-of-state, alpha is:

$$\alpha_i = \frac{1}{T_{ri}^{1/2}} \tag{4}$$

It was not referred to as alpha but equation 4 was incorporated into equation 1.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
PC	p_{ci}	—	—	10^5	10^8	PRESSURE

Soave Modification

The parameter α is a temperature function introduced by Soave in the Redlich-Kwong equation-of-state to improve the correlation of the pure component vapor pressure:

$$\alpha_i(T) = [1 + m_i(1 - T_{ri}^{1/2})]^2 \tag{5}$$

Equation 3 still holds. The parameter m_i can be correlated with the acentric factor:

$$m_i = 0.48 + 1.57\omega_i - 0.176\omega_i^2 \tag{6}$$

Equations 1, 2, 3, 5 and 6 are the standard Redlich-Kwong-Soave formulation.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCRKS	T_{ci}	TC	X	5.0	2000.0	TEMPERATURE
PCRKS	p_{ci}	PC	X	10^5	10^8	PRESSURE
OMGRKS	ω_i	OMEGA	X	-0.5	2.0	—

Boston-Mathias Extrapolation

For light gases at high reduced temperatures (> 5), equation 4 gives unrealistic results. The boundary conditions are that attraction between molecules should vanish for extremely high temperatures, and α reduces asymptotically to zero. Boston and Mathias derived an alternative function for temperatures higher than critical:

$$\alpha_i(T) = [\exp[c_i(1 - T_{ri}^{d_i})]]^2 \tag{7}$$

With

$$d_i \quad = \quad 1 + \frac{m_i}{2}$$

$$c_i \quad = \quad 1 - \frac{1}{d_i}$$

Where:

m_i =   Computed by equation 6

Equation 5   =   Used for subcritical temperatures

Additional parameters are not needed.

Mathias Alpha Function

In equation 4, m_i is a constant for each component. For high accuracy or for highly curved vapor pressure behavior as a function of temperature, such as with polar compounds, the Mathias function is more flexible:

$$\alpha_i(T) = [1 + m_i(1 - T_{ro}^{\frac{1}{2}}) - \eta_i(1 - T_{ri}^{\frac{1}{2}})(0.7 - T_{ri})]^2 \tag{8}$$

For $\eta_i = 0$, equation 8 reduces to the standard Redlich-Kwong-Soave formulation, including equation 6 for m_i. For temperatures above critical, the Boston-Mathias extrapolation is used, that is, equation 6 with:

$$d_i = 1 + \frac{m_i}{2} + 0.3\eta_i \tag{9}$$

$$c_i = 1 - \frac{1}{d_i} \qquad (10)$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCRKA	T_{ci}	TC	X	5.0	2000.0	TEMPERATURE
PCRKA	p_{ci}	PC	X	10^5	10^8	PRESSURE
OMGRKA	ω_i	OMEGA	X	-0.5	2.0	—
RKAPOL	η_i	—	X	-2.0	2.0	—

Extended Mathias Alpha Function

An extension of the Mathias approach is:

$$\alpha_i(T) = [1 + m_i(1 - T_{ri}^{1/2}) - p_{1,i}(1 - T_{ri}^{1/2})(1 + p_{2,i}T + p_{3,i}T_{ri}^2)]^2 \quad (11)$$

Where m_i is computed by equation 6. If the polar parameters $p_{1,i}$, $p_{2,i}$ and $p_{3,i}$ are zero, equation 11 reduces to the standard Redlich-Kwong-Soave formulation. You can use vapor pressure data to regress the constants if the temperature is subcritical. Equation 11 is used only for temperatures below critical.

The Boston-Mathias extrapolation is used for temperatures above critical, that is, with:

$$d_i = \tfrac{1}{2} m_i - p_{1,i}\left(1 + p_{2,i} + p_{3,i}\right) \qquad (12)$$

$$c_i = 1 - \frac{1}{d_i} \qquad (13)$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCRKU	T_{ci}	TC	X	5.0	2000.0	TEMPERATURE
PCRKU	p_{ci}	PC	X	10^5	10^8	PRESSURE
OMGRKU	ω_i	OMEGA	X	-0.5	2.0	—
RKUPP0	$p_{1,i}$	—	X	—	—	—
RKUPP1	$p_{2,i}$	0	X	—	—	—
RKUPP2	$p_{3,i}$	0	X	—	—	—

Mathias-Copeman Alpha Function

The Mathias-Copeman Alpha Function approach is another extension of the Mathias approach. For high accuracy or strongly curved vapor pressure behavior as a function of temperature, the Mathias-Copeman function is highly flexible:

$$\alpha_i(T) = [1 + m_i(1 - T_{ri}^{\frac{1}{2}}) + c_{2,i}(1 - T_{ri}^{\frac{1}{2}})^2 + c_{3,i}(1 - T_{ri}^{\frac{1}{2}})^3]^2 \qquad (14)$$

For $c_{2,i} = 0$ and $c_{3,i} = 0$ this expression reduces to the standard Redlich-Kwong-Soave formulation if $c_{1,i} = m_i$. If the temperature is subcritical, use vapor pressure data to regress the constants. If the temperature is supercritical, set $c_{2,i}$ and $c_{3,i}$ to 0.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCRKS	T_{ci}	TC	X	5.0	2000.0	TEMPERATURE
PCRKS	p_{ci}	PC	X	10^5	10^8	PRESSURE
RKSMCP/1	$c_{1,i}$	—	X	—	—	—
RKSMCP/2	$c_{2,i}$	0	X	—	—	—
RKSMCP/3	$c_{3,i}$	0	X	—	—	—

Schwartzentruber-Renon-Watanasiri Alpha Function

This method combines the flexibility of the Mathias-Copeman approach and the correction for high reduced temperatures by Boston and Mathias:

$$\alpha_i(T) = [1 + m_i(1 - T_{ri}^{\frac{1}{2}}) - (1 - T_{ri})(p_{1,i} + p_{2,i}T_{ri} + p_{3,i}T_{ri}^2)]^2 \qquad (15)$$

Where m_i is computed by equation 6 and the polar parameters $p_{1,i}$, $p_{2,i}$ and $p_{3,i}$ are comparable with the c parameters of the Mathias-Copeman expression. Equation 15 reduces to the standard Redlich-Kwong-Soave formulation if the polar parameters are zero. Use vapor pressure data to regress the constants if the temperature is subcritical. Equation 15 is very similar to the extended Mathias equation, but it is easier to use in data regression. It is used only for temperatures below critical. The Boston-Mathias extrapolation is used for temperatures above critical, that is, use equation 6 with:

$$d_i = 1 + \frac{m_i}{2} - (p_{1,i} + p_{2,i} + p_{3,i}) \qquad (16)$$

$$c_i = 1 - \frac{1}{d_i} \qquad (17)$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCPR	T_{ci}	TC	X	5.0	2000.0	TEMPERATURE
PCPR	p_{ci}	PC	X	10^5	10^8	PRESSURE
OMGPR	ω_i	OMEGA	X	-0.5	2.0	—
RKSSRP/1	$p_{1,i}$	—	X	—	—	—
RKSSRP/2	$p_{2,i}$	0	X	—	—	—
RKSSRP/3	$p_{3,i}$	0	X	—	—	—

Use of Alpha Functions

The use of alpha functions in Soave-Redlich-Kwong based equation-of-state models is given in the following table. You can verify and change the value of possible option codes on the Properties Property Method Model form.

Alpha Function	Model Name	First Option Code
original RK	ESRK0, ESRK	—
standard RKS	ESRKSTD0, ESRKSTD	—
standard RKS/Boston-Mathias	ESRKS0, ESRKS0	—
	ESRKSWS0, ESRKSWS	1
	ESRKSV10, ESRKV1	1
	ESRKSV20, ESRKSV2	1
Mathias/Boston-Mathias	ESRKA0, ESRKA	—
Extended Mathias/Boston-Mathias	ESRKU0, ESRKU	—
Mathias-Copeman	ESRKSW0, ESRKSW	2
	ESRKSV10, ESRKSV1	2
	ESRKSV20, ESRKSV2	2
Schwartzentruber-Renon-Watanasiri	ESPRWS0, ESPRWS	3 (default)
	ESRKSV10, ESRKSV1	3 (default)
	ESRKSV20, ESRKSV2	3 (default)

References

J. F. Boston and P.M. Mathias, "Phase Equilibria in a Third-Generation Process Simulator" in Proceedings of the 2nd International Conference on Phase Equilibria and Fluid Properties in the Chemical Process Industries, West Berlin, (17-21 March 1980), pp. 823-849.

P. M. Mathias, "A Versatile Phase Equilibrium Equation-of-state", Ind. Eng. Chem. Process Des. Dev., Vol. 22, (1983), pp. 385–391.

P.M. Mathias and T.W. Copeman, "Extension of the Peng-Robinson Equation-of-state To Complex Mixtures: Evaluation of

the Various Forms of the Local Composition Concept", Fluid Phase Eq., Vol. 13, (1983), p. 91.

O. Redlich and J. N. S. Kwong, "On the Thermodynamics of Solutions V. An Equation-of-state. Fugacities of Gaseous Solutions," Chem. Rev., Vol. 44, (1949), pp. 223–244.

J. Schwartzentruber and H. Renon, "Extension of UNIFAC to High Pressures and Temperatures by the Use of a Cubic Equation-of-state," Ind. Eng. Chem. Res., Vol. 28, (1989), pp. 1049–1055.

J. Schwartzentruber, H. Renon, and S. Watanasiri, "K-values for Non-Ideal Systems:An Easier Way," Chem. Eng., March 1990, pp. 118-124.

G. Soave, "Equilibrium Constants for a Modified Redlich-Kwong Equation-of-state," Chem Eng. Sci., Vol. 27, (1972), pp. 1196-1203.

Huron-Vidal Mixing Rules   Huron and Vidal (1979) used a simple thermodynamic relationship to equate the excess Gibbs energy to expressions for the fugacity coefficient as computed by equations of state:

$$G_m^E = RT \ln \varphi - \sum_i x_i RT \ln \varphi_i^* \tag{1}$$

Equation 1 is valid at any pressure, but cannot be evaluated unless some assumptions are made. If Equation 1 is evaluated at infinite pressure, the mixture must be liquid-like and extremely dense. It can be assumed that:

$$V(p = \infty) = b \tag{2}$$

$$V^E(p = \infty) = 0 \tag{3}$$

Using equations 2 and 3 in equation 1 results in an expression for a/b that contains the excess Gibbs energy at an infinite pressure:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{1}{\Lambda} G_m^E(p = \infty) \tag{4}$$

Where:

$$\Lambda = \frac{1}{\lambda_1 - \lambda_2} \ln\left(\frac{1 + \lambda_1}{1 + \lambda_2}\right) \tag{5}$$

The parameters λ_1 and λ_2 depend on the equation-of-state used. In general a cubic equation-of-state can be written as:

$$p = \frac{RT}{(V_m - b)} - \frac{a}{(V + \lambda_1 b)(V_m + \lambda_2 b)} \tag{6}$$

Values for λ_1 and λ_2 for the Peng-Robinson and the Soave-Redlich-Kwong equations of state are:

Equation-of-state	λ_1	λ_2
Peng-Robinson	$1 - \sqrt{2}$	$1 + \sqrt{2}$
Redlich-Kwong-Soave	1	0

This expression can be used at any pressure as a mixing rule for the parameter. The mixing rule for b is fixed by equation 3. Even when used at other pressures, this expression contains the excess Gibbs energy at infinite pressure. You can use any activity coeffecient model to evaluate the excess Gibbs energy at infinite pressure. Binary interaction coefficients must be regressed. The mixing rule used contains as many binary parameters as the activity coefficient model chosen.

This mixing rule has been used successfully for polar mixtures at high pressures, such as systems containing light gases. In theory, any activity coefficient model can be used. But the NRTL equation (as modified by Huron and Vidal) has demonstrated better performance.

The Huron-Vidal mixing rules combine extreme flexibility with thermodynamic consistency, unlike many other mole-fraction-dependent equation-of-state mixing rules. The Huron-Vidal mixing rules do not allow flexibility in the description of the excess molar volume, but always predict reasonable excess volumes.

The Huron-Vidal mixing rules are theoretically incorrect for low pressure, because quadratic mole fraction dependence of the second virial coefficient (if derived from the equation-of-state) is not preserved. Since equations of state are primarily used at high pressure, the practical consequences of this drawback are minimal.

The Gibbs energy at infinite pressure and the Gibbs energy at an arbitrary high pressure are similar. But the correspondence is not close enough to make the mixing rule predictive.

There are several methods for modifying the Huron-Vidal mixing rule to make it more predictive. The following three methods are used in Aspen Physical Property System equation-of-state models:

- The modified Huron-Vidal mixing rule, second order approximation (MHV2)
- The Predictive SRK Method (PSRK)
- The Wong-Sandler modified Huron-Vidal mixing rule (WS)

These mixing rules are discussed separately in the following sections. They have major advantages over other composition-dependent equation-of-state mixing rules.

M.- J. Huron and J. Vidal, "New Mixing Rules in Simple Equations of State for representing Vapour-liquid equilibria of strongly non-ideal mixtures," Fluid Phase Eq., Vol. 3, (1979), pp. 255-271.

MHV2 Mixing Rules

Dahl and Michelsen (1990) use a thermodynamic relationship between excess Gibbs energy and the fugacity computed by equations of state. This relationship is equivalent to the one used by Huron and Vidal:

$$\frac{G_m^E}{RT} = \ln\left(\frac{f}{RT}\right) - \sum_i x_i \ln\left(\frac{f_i}{RT}\right) \tag{1}$$

The advantage is that the expressions for mixture and pure component fugacities do not contain the pressure. They are functions of compacity V/b and α:

$$\ln\left(\frac{f_i^*}{RT}\right) + \ln b_i = Q\left(\frac{V_i^*}{b_i}, \alpha_i\right) \tag{2}$$

Where:

$$\alpha_i = \frac{a_i}{b_i RT} \tag{3}$$

and

$$\ln\left(\frac{f}{RT}\right) + \ln b_i = Q\left(\frac{V_m}{b}, \alpha\right) \tag{4}$$

With:

$$\alpha = \frac{a}{bRT} \tag{5}$$

The constants λ_1 and λ_2, which depend only on the equation-of-state (see Huron-Vidal Mixing Rules, this chapter) occur in equations 2 and 4.

Instead of using infinite pressure for simplification of equation 1, the condition of zero pressure is used. At p= 0 an exact relationship between the compacity and α can be derived. By substitution the simplified equation $q(\alpha)$ is obtained, and equation 1 becomes:

$$\frac{G_m^E(p=0)}{RT} + \sum_i x_i \ln\left(\frac{b_i}{b}\right) = q(\alpha) - \sum_i x_i q(\alpha_i) \tag{6}$$

However, $q(\alpha)$ can only be written explicitly for $\alpha = 5.8$. Only an approximation is possible below that threshold. Dahl and

Michelsen use a second order polynomial fitted to the analytical solution for $10 < \alpha < 13$ that can be extrapolated to low alpha:

$$q(\alpha) = q_i\alpha + q_2\alpha^2 \tag{7}$$

Since $q(\alpha)$ is a universal function (for each equation-of-state), the combination of equations 6 and 7 form the MHV2 mixing rule. Excess Gibbs energies, from any activity coefficient model with parameters optimized at low pressures, can be used to determine α, if α_i, b_i, and b are known. To compute b, a linear mixing rule is assumed as in the original Huron-Vidal mixing rules:

$$b = \sum_i x_i b_i \tag{8}$$

This equation is equivalent to the assumption of zero excess molar volume.

The MHV2 mixing rule was the first successful predictive mixing rule for equations of state. This mixing rule uses previously determined activity coefficient parameters for predictions at high pressures. UNIFAC was chosen as a default for its predictive character. The Lyngby modified UNIFAC formulation was chosen for optimum performance (see UNIFAC (Lyngby Modified)). However, any activity coefficient model can be used when its binary interaction parameters are known.

Like the Huron-Vidal mixing rules, the MHV2 mixing rules are not flexible in the description of the excess molar volume. The MHV2 mixing rules are theoretically incorrect at the low pressure limit. But the practical consequences of this drawback are minimal (see Huron-Vidal Mixing Rules, this chapter).

S. Dahl and M.L. Michelsen, "High-Pressure Vapor-Liquid Equilibrium with a UNIFAC-based Equation-of-state," AIChE J., Vol. 36, (1990), pp. 1829-1836.

Predictive Soave-Redlich-Kwong-Gmehling Mixing Rules

These mixing rules by Holderbaum and Gmehling (1991) use a relationship between the excess Helmholtz energy and equation-of-state. They do not use a relationship between equation-of-state properties and excess Gibbs energy, as in the Huron-Vidal mixing rules. The pressure-explicit expression for the equation-of-state is substituted in the thermodynamic equation:

$$p = -\left(\frac{\partial A}{\partial V}\right)_T \tag{1}$$

The Helmholtz energy is calculated by integration. A^E is obtained by:

$$A_m^E = A_m - \sum_i x_i A_i^* - RT \sum_I x_i \ln x_i \tag{2}$$

Where both A_i^* and A_m are calculated by using equation 1. A_i^* and A_m are written in terms of equation-of-state parameters.

The simplification of constant packing fraction (V_m / b) is used:

$$\frac{V_i^{*,l}}{b_i} = \frac{V_m^l}{b} \tag{3}$$

With:

$$b = \sum_i x_i b_i \tag{4}$$

Therefore:

$$V_m^E(p = \infty) = 0 \tag{5}$$

The mixing rule is:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{1}{\Lambda'} A_m^E(p) \tag{6}$$

Where Λ' is slightly different from Λ for the Huron-Vidal mixing rule:

$$\Lambda' = \frac{1}{\lambda_1 - \lambda_2} \ln \left(\frac{\dfrac{V_m}{b} + \lambda L_1}{\dfrac{V_m}{b} + \lambda_2} \right) \tag{7}$$

Where λ_1 and λ_2, depend on the equation-of-state (see Huron-Vidal Mixing Rules, this chapter). If equation 6 is applied at infinite pressure, the packing fraction goes to 1. The excess Helmholtz energy is equal to the excess Gibbs energy. The Huron-Vidal mixing rules are recovered.

The goal of these mixing rules is to be able to use binary interaction parameters for activity coefficient models at any pressure. These parameters have been optimized at low pressures. UNIFAC is chosen for its predictive character. Two issues exist: the packing fraction is not equal to one, and the excess Gibbs and Helmholtz energy are not equal at the low pressure where the UNIFAC parameters have been derived.

Fischer (1993) determined that boiling point, the average packing fraction for about 80 different liquids with different chemical natures was 1.1. Adopting this value, the difference between liquid

excess Gibbs energy and liquid excess Helmholtz energy can be computed as:

$$A_m^{E,l}(p) = G_m^{E,l}(p = 1atm) + \int_{V_m^l=1.1b}^{V_m^l=b} pdV_m^l - \sum_i x_i \int_{V_i^{*,l}=1.1b}^{V_i^{*,l}=b} pdV_i^{*,l} \quad (8)$$

The result is a predictive mixing rule for cubic equations of state. But the original UNIFAC formulation gives the best performance for any binary pair with interactions available from UNIFAC. Gas-solvent interactions are unavailable.

At the University of Oldenburg in Germany, the UNIFAC groups were extended with often-occurring gases. New group interactions were determined from gas-solvent data, specific to the Redlich-Kwong-Soave equation-of-state. The new built-in parameters to the Aspen Physical Property System are activated when using the PSRK equation-of-state model.

The PSRK method has a lot in common with the Huron-Vidal mixing rules. The mole fraction is dependent on the second virial coefficient and excess volume is predicted. These are minor disadvantages.

T. Holderbaum and J. Gmehling, "PSRK: A Group Contribution Equation-of-state based on UNIFAC," Fluid Phase Eq., Vol. 70, (1991), pp. 251-265.

K. Fischer, "Die PSRK-Methode: Eine Zustandsgleichung unter Verwendung des UNIFAC-Gruppenbeitragsmodells," (Düsseldorf: VDI Fortschrittberichte, Reihe 3: Verfahrenstechnik, Nr. 324, VDI Verlag GmbH, 1993).

Wong-Sandler Mixing Rules

These mixing rules use a relationship between the excess Helmholtz energy and equation-of-state. They do not use a relationship between equation-of-state properties and excess Gibbs energy, as in the Huron-Vidal mixing rules. The pressure-explicit expression for the equation-of-state is substituted in the thermodynamic equation:

$$p = -\left(\frac{\partial A}{\partial V}\right)_T \quad (1)$$

The Helmholtz energy is obtained by integration, A^E is obtained by:

$$A_m^E = A_m - \sum_i x_i A_i^* - RT \sum_i x_i \ln x_i \quad (2)$$

Where both A_i^* and A_m are calculated by using equation 1. A_i^* and A_m are written in terms of equation-of-state parameters.

Like Huron and Vidal, the limiting case of infinite pressure is used. This simplifies the expressions for A_i^* and A_m. Equation 2 becomes:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{1}{\Lambda} A_m^E (p = \infty) \tag{3}$$

Where Λ depends on the equation-of-state (see Huron-Vidal Mixing Rules, this chapter).

Equation 3 is completely analogous to the Huron-Vidal mixing rule for the excess Gibbs energy at infinite pressure. (See equation 4, Huron-Vidal Mixing Rules., this chapter.) The excess Helmholtz energy can be approximated by the excess Gibbs energy at low pressure from any liquid activity coefficient model. Using the Helmholtz energy permits another mixing rule for b than the linear mixing rule. The mixing rule for b is derived as follows. The second virial coefficient must depend quadratically on the mole fraction:

$$B(T) = \sum_i \sum_j x_i x_j B_{ij} \tag{4}$$

With:

$$B_{ij} = \frac{(B_{ii} + B_{jj})}{2}(1 - k_{ij}) \tag{5}$$

The relationship between the equation-of-state at low pressure and the virial coefficient is:

$$B = b - \frac{a}{RT} \tag{6}$$

$$B_{ii} = b_i - \frac{a_i}{RT} \tag{7}$$

Wong and Sandler discovered the following mixing rule to satisfy equation 4 (using equations 6 and 7):

$$b = \frac{\displaystyle\sum_i \sum_j x_i x_j B_{ij}}{1 - \dfrac{A_m^E(p = \infty)}{\Lambda RT} - \displaystyle\sum_i x_i B_{ij}}$$

The excess Helmholtz energy is almost independent of pressure. It can be approximated by the Gibbs energy at low pressure. The difference between the two functions is corrected by fitting k_{ij} until the excess Gibbs energy from the equation-of-state (using the mixing rules 3 and 8) is equal to the excess Gibbs energy

computed by an activity coeffecient model. This is done at a specific mole fraction and temperature.

This mixing rule accurately predicts the VLE of polar mixtures at high pressures. UNIFAC or other activity coeffecient models and parameters from the literature are used. Gas solubilities are not predicted. They must be regressed from experimental data.

Unlike other (modified) Huron-Vidal mixing rules, the Wong and Sandler mixing rule meets the theoretical limit at low pressure. The use of k_{ij} does influence excess molar volume behavior. For calculations where densities are important, check whether they are realistic.

References

D. S. Wong and S. I. Sandler, "A Theoretically Correct New Mixing Rule for Cubic Equations of State for Both Highly and Slightly Non-ideal Mixtures," AIChE J., Vol. 38, (1992), pp. 671 – 680.

D. S. Wong, H. Orbey, and S. I. Sandler, "Equation-of-state Mixing Rule for Non-ideal Mixtures Using Available Activity Coefficient Model Parameters and That Allows Extrapolation over Large Ranges of Temperature and Pressure", Ind Eng Chem. Res., Vol. 31, (1992), pp. 2033 – 2039.

H. Orbey, S. I. Sandler and D. S. Wong, "Accurate Equation-of-state Predictions at High Temperatures and Pressures Using the Existing UNIFAC Model," Fluid Phase Eq., Vol. 85, (1993), pp. 41 – 54.

Activity Coefficient Models

The Aspen Physical Property System has 18 built-in activity coefficient models. This section describes the activity coefficient models available.

Model	Type
Bromley-Pitzer	Electrolyte
Chien-Null	Regular solution, local composition
Constant Activity Coefficient	Arithmetic
Electrolyte NRTL	Electrolyte
Ideal Liquid	Ideal
NRTL (Non-Random-Two-Liquid)	Local composition
Pitzer	Electrolyte
Polynomial Activity Coefficient	Arithmetic
Redlich-Kister	Arithmetic
Scatchard-Hildebrand	Regular solution
Three-Suffix Margules	Arithmetic
UNIFAC	Group contribution
UNIFAC (Lyngby modified)	Group contribution
UNIFAC (Dortmund modified)	Group contribution
UNIQUAC	Local composition
Van Laar	Regular solution
Wagner interaction parameter	Arithmetic
Wilson	Local composition
Wilson with Liquid Molar Volume	Local composition

Bromley-Pitzer Activity Coefficient Model

The Bromley-Pitzer activity coefficient model is a simplified Pitzer activity coefficient model with Bromley correlations for the interaction parameters. See Appendix A for a detailed description. This model has predictive capabilities. It can be used up to 6M ionic strength, but is less accurate than the Pitzer model if the parameter correlations are used.

The Bromley-Pitzer model in the Aspen Physical Property System involves user-supplied parameters, used in the calculation of binary parameters for the electrolyte system.

Parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$ and θ have five elements to account for temperature dependencies. Elements P1 through P5 follow the temperature dependency relation:

$$f(T) = P_1 + P_2(T - T^{ref}) + P_3\left(\frac{1}{T} - \frac{1}{T^{ref}}\right) + P_4 \ln\left(\frac{T}{T^{ref}}\right) + P_5(T^2 - (T^{ref})^2)$$

Where:

T^{ref} =   298.15K

The user must:

- Supply these elements using a Properties Parameters Binary.T-Dependent form.
- Specify Comp ID i and Comp ID j on this form, using the same order that appears on the Components Specifications Selection sheet form.

Parameter Name	Symbol	No. of Elements	Default	Units
Ionic Unary Parameters				
GMBPB	β_{ion}	1	0	—
GMBPD	$\delta_{ion} 1$	1	0	—
Cation-Anion Parameters				
GMBPB0	$\beta^{(0)}$	5	0	—
GMBPB1	$\beta^{(1)}$	5	0	—
GMBPB2	$\beta^{(2)}$	5	0	—
GMBPB3	$\beta^{(3)}$	5	0	—
Cation-Cation Parameters				
GMBPTH	$\theta_{cc'}$	5	0	—
Anion-Anion Parameters				
GMBPTH	$\theta_{aa'}$	5	0	—
Molecule-Ion and Molecule-Molecule Parameters				
GMBPB0	$\beta^{(0)}$	5	0	—
GMBPB1	$\beta^{(1)}$	5	0	—

Chien-Null

The Chien-Null model calculates liquid activity coefficients and it can be used for highly non-ideal systems. The generalized expression used in its derivation can be adapted to represent other well known formalisms for the activity coefficient by properly defining its binary terms. This characteristic allows the model the use of already available binary parameters regressed for those other liquid activity models with thermodynamic consistency.

The equation for the Chien-Null liquid activity coeficient is:

$$\ln \gamma_i = \frac{1}{2}\left[\frac{\sum_j A_{ji}x_i \sum_j R_{ji}x_j}{\sum_j S_{ji}x_j \sum_j V_{ji}x_j} + \sum_k x_k \frac{\sum_j A_{jk}x_i \sum_j R_{jk}x_j}{\sum_j S_{jk}x_j \sum_j V_{jk}x_j}\left(\frac{A_{ik}}{\sum_j A_{jk}x_j} + \frac{R_{ik}}{\sum_j R_{jk}x_j} - \frac{S_{ik}}{\sum_j S_{jk}x_j} - \frac{V_{ik}}{\sum_j V_{jk}x_j}\right)\right]$$

Where:

$$R_{ji} = \frac{A_{ji}}{A_{ij}}$$

$$A_{ii} = 0$$

$$\frac{A_{ji}}{A_{ij}} = 1$$

$$A_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

Subscripts i and j are component indices.

The choice of model and parameters can be set for each binary pair constituting the process mixture by assigning the appropriate value to the ICHNUL parameter.

The Regular Solution and Scatchard-Hamer models are regained by substituting in the general expression (ICHNUL = 1 or 2).

$$V_{ji} = S_{ji} = \frac{V_j^{*,l}}{V_i^{*,l}}$$

Where:

$V_j^{*,l}$ = Liquid molar volume of component i

The Chien-Null activity coefficient model collapses to the Margules liquid activity coefficient expression by setting (ICHNUL = 3):

$$V_{ji} = S_{ji} = 1$$

The Van Laar Liquid activity coefficient model is the obtained when the V and S parameters in the Chien-Null models are set to the ratio of the cross terms of A (ICHNUL = 4:)

$$V_{ji} = S_{ji} = \frac{A_{ji}}{A_{ij}}$$

Finally, the Renon or NRTL model is obtained when we make the following susbstitutions in the Chien-Null expression for the liquid activity (ICHNUL = 5).

$$S_{ji} = R_{ji} \frac{A_{ji}}{A_{ij}}$$

$$A_{ji} = 2\tau_{ji}G_{ji}$$

$$V_{ji} = G_{ji}$$

The following are defined for the Non-Random Two-Liquid activity coefficient model, where:

$$G_{ji} = e^{(-C_{ji}\tau_{ji})}$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

$$C_{ij} = c_{ij} + d_{ij}(T - 273.15K)$$

$$c_{ji} = c_{ij}$$

$$d_{ji} = d_{ij}$$

The binary parameters CHNULL/1, CHNULL/2, and CHNULL/3 can be determined from regression of VLE and/or LLE data. Also, if you have parameters for many of the mixture pairs for the Margules, Van Laar, Scatchard-Hildebrand, and NRTL (Non-Random-Two-Liquid) activity models, you can use them directly with the Chien-Null activity model after selecting the proper code (ICHNUL) to identify the source model and entering the appropriate activity model parameters.

Parameter Name/Element	Symbol	Default	Upper Limit	Lower Limit	Units
ICHNUL	—	3	1	6	—
CHNULL/1	a_{ij}	0	—	—	—
CHNULL/2	b_{ij}	0	—	—	—
CHNULL/3	Vij	0	—	—	—

The parameter ICHNUL is used to identify the activity model parameters available for each binary pair of interest. The following values are allowed for ICHNUL:

ICHNUL = 1 or 2, sets the model to the Scatchard-Hamer or regular solution model for the associated binary;

ICHNUL = 3, sets the model to the Three-Suffix Margules activity model for the associated binary;

ICHNUL = 4, sets the model to the Van Laar formalism for the activity model for the associated binary;

ICHNUL = 5, sets the model to the NRTL (Renon) formalism for the activity model for the associated binary.

ICHNUL = 6, sets the model to the full Chien-Null formalism for the activity model for the associated binary.

When you specify a value for the ICHNUL parameter that is different than the default, you must enter the appropriate binary model parameters for the chosen activity model directly. The routine will automatically convert the expressions and parameters to conform to the Chien-Null formulation.

Constant Activity Coefficient

This approach is used exclusively in metallurgical applications where multiple liquid and solid phases can coexist. You can assign any value to the activity coefficient of component i. Use the Properties Parameters Unary.Scalar form.
The equation is:

$$\gamma_i = a_i$$

Parameter Name/Element	Symbol	Default	MDS	Upper Limit	Lower Limit	Units
GMCONS	a_i	1.0	x	—	—	—

Electrolyte NRTL Activity Coefficient Model

The Aspen Physical Property System uses the electrolyte NRTL model to calculate activity coefficients, enthalpies, and Gibbs energies for electrolyte systems. Model development and working equations are provided in Appendix B.

The adjustable parameters for the electrolyte NRTL model include the:

- Pure component dielectric constant coefficient of nonaqueous solvents
- Born radius of ionic species
- NRTL parameters for molecule-molecule, molecule-electrolyte, and electrolyte-electrolyte pairs

The pure component dielectric constant coefficients of nonaqueous solvents and Born radius of ionic species are required only for mixed-solvent electrolyte systems. The temperature dependency of the dielectric constant of solvent B is:

$$\varepsilon_B(T) = A_B + B_B\left(\frac{1}{T} - \frac{1}{C_B}\right)$$

Each type of electrolyte NRTL parameter consists of both the nonrandomness factor, α, and energy parameters, τ. The temperature dependency relations of the electrolyte NRTL parameters are:

- Molecule-Molecule Binary Parameters:

$$\tau_{BB'} = A_{BB'} + \frac{B_{BB'}}{T} + F_{BB'}\ln(T) + G_{BB'}T$$

- Electrolyte-Molecule Pair Parameters:

$$\tau_{ca,B} = C_{ca,B} + \frac{D_{ca,B}}{T} + E_{ca,B}\left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right)\right]$$

$$\tau_{B,ca} = C_{B,ca} + \frac{D_{B,ca}}{T} + E_{B,ca}\left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right)\right]$$

- Electrolyte-Electrolyte Pair Parameters:

For the electrolyte-electrolyte pair parameters, the two electrolytes must share either one common cation or one common anion:

$$\tau_{c'a,c''a} = C_{c'a,c''a} + \frac{D_{c'a,c''a}}{T} + E_{c'a,c''a}\left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right)\right]$$

$$\tau_{ca',ca''} = C_{ca',ca''} + \frac{D_{ca',ca''}}{T} + E_{ca',ca''}\left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right)\right]$$

Where:

$$T^{ref} \quad = \quad 298.15K$$

Many parameter pairs are included in the electrolyte NRTL model parameter databank (see Physical Property Data, Chapter 1).

Parameter Name	Symbol	No. of Elements	Default	MDS	Units
Dielectric Constant Unary Parameters					
CPDIEC	A_B	1	—	—	—
	B_B	1	0	—	—
	C_B	1	298.15	—	TEMPERATURE
Ionic Born Radius Unary Parameters					
RADIUS	r_i	1	3×10^{-10}	—	LENGTH
Molecule-Molecule Binary Parameters					
NRTL/1	A_{BB}	—	0	x	—
	$A_{B'B}$	—	0	x	—
NRTL/2	$B_{BB'}$	—	0	x	TEMPERATURE
	$B_{B'B}$	—	0	x	TEMPERATURE
NRTL/3	$\alpha_{BB'} = \alpha_{B'B}$	—	.3	x	—

NRTL/4	—	—	0	x	TEMPERATURE
NRTL/5	$F_{BB'}$	—	0	x	TEMPERATURE
	$F_{B'B}$	—	0	x	TEMPERATURE
NRTL/6	$G_{BB'}$	—	0	x	TEMPERATURE
	$G_{B'B}$	—	0	x	TEMPERATURE

Electrolyte-Molecule Pair Parameters

GMELCC	$C_{ca,B}$	1	0	x	—
	$C_{B,ca}$	1	0	x	—
GMELCD	$D_{ca,B}$	1	0	x	TEMPERATURE
	$D_{B,ca}$	1	0	x	TEMPERATURE
GMELCE	$E_{ca,B}$	1	0	x	—
	$E_{B,ca}$	1	0	x	—
GMELCN	$\alpha_{ca,B} = \alpha_{B,ca}$	1	.2	x	—

Electrolyte-Electrolyte Pair Parameters

GMELCC	$C_{ca',ca''}$	1	0	x	—
	$C_{ca'',ca'}$	1	0	x	—
	$C_{c'a,c''a}$	1	0	x	—
	$C_{c''a,c'a}$	1	0	x	—
GMELCD	$D_{ca',ca''}$	1	0	x	TEMPERATURE
	$D_{ca'',ca'}$	1	0	x	TEMPERATURE
	$D_{c'a,c''a}$	1	0	x	TEMPERATURE
	$D_{c''a,c'a}$	1	0	x	TEMPERATURE
GMELCE	$E_{ca',ca''}$	1	0	x	—
	$E_{ca'',ca'}$	1	0	x	—
	$E_{c'a,c''a}$	1	0	x	—
	$E_{c''a,c'a}$	1	0	x	—
GMELCN	$\alpha_{ca',ca''} = \alpha_{ca'',ca'}$	1	.2	x	—
	$\alpha_{c'a,c''a} = \alpha_{c''a,c'a}$	1	.2	x	—

Ideal Liquid　　This model is used in Raoult's law. It represents ideality of the liquid phase. This model can be used for mixtures of hydrocarbons of similar carbon number. It can be used as a reference to compare the results of other activity coefficient models.

The equation is:

$$\ln \gamma_i = 0$$

NRTL (Non-Random Two-Liquid)

The NRTL model calculates liquid activity coefficients for the following property methods: NRTL, NRTL-2, NRTL-HOC, NRTL-NTH, and NRTL-RK. It is recommended for highly non-ideal chemical systems, and can be used for VLE and LLE applications. The model can also be used in the advanced equation-of-state mixing rules, such as Wong-Sandler and MHV2.

The equation for the NRTL model is:

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right)$$

Where:

G_{ij}	=	$\exp(-\alpha_{ij} \tau_{ij})$
τ_{ij}	=	$a_{ij} + {b_{ij}}/{T} + e_{ij} \ln T + f_{ij} T$
α_{ij}	=	$c_{ij} + d_{ij}(T - 273.15K)$
τ_{ii}	=	0
G_{ii}	=	1
a_{ij}	?	a_{ji}
b_{ij}	?	b_{ji}
c_{ij}	?	c_{ji}
d_{ij}	?	d_{ji}

Recommended c_{ij} Values for Different Types of Mixtures

c_{ij}	Mixtures
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

The binary parameters a_{ij}, b_{ij}, c_{ij}, d_{ij}, e_{ij}, and f_{ij} can be determined from VLE and/or LLE data regression. The Aspen Physical Property System has a large number of built-in binary parameters for the NRTL model. The binary parameters have been

regressed using VLE and LLE data from the Dortmund Databank. The binary parameters for the VLE applications were regressed using the ideal gas, Redlich-Kwong, and Hayden O'Connell equations of state. See Physical Property Data, Chapter 1, for details.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
NRTL/1	a_{ij}	0	x	-100.0	100.0	—
NRTL/2	b_{ij}	0	x	-30000	30000.0	TEMPERATURE
NRTL/3	c_{ij}	0.30	x	0.0	1.0	—
NRTL/4	d_{ij}	0	x	-0.02	0.02	TEMPERATURE
NRTL/5	e_{ij}	0	x	—	—	TEMPERATURE
NRTL/6	f_{ij}	0	x	—	—	TEMPERATURE

References

H. Renon and J.M. Prausnitz, "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures," AIChE J., Vol. 14, No. 1, (1968), pp. 135 – 144.

Pitzer Activity Coefficient Model

The Pitzer model is commonly used in the calculation of activity coefficients for aqueous electrolytes up to 6 molal ionic strength. Do not use this model if a non-aqueous solvent exists. The model development and working equations are provided in Appendix C. Parameter conversion between the Pitzer notation and our notation is also provided.

The Pitzer model in the Aspen Physical Property System involves user-supplied parameters that are used in the calculation of binary and ternary parameters for the electrolyte system.

Five elements (P1 through P5) account for the temperature dependencies of parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$, c^{φ}, and θ. These parameters follow the temperature dependency relation:

$$f(T) = P_{1i} + P_{2i}(T - T^{ref}) + P_{3i}\left(\frac{1}{T} - \frac{1}{T^{ref}}\right) + P_{4i}\ln\left(\frac{T}{T^{ref}}\right) + P_{5i}\left(T^2 - \left(T^{ref}\right)^2\right)$$

Where:

Tref   =   298.15 K

The user must:

- Supply these elements using a Properties Parameters Binary.T-Dependent form.
- Specify Comp ID i and Comp ID j on this form, using the same order that appears on the Components Specifications Selection sheet form.

The parameters are summarized in the following table. There is a Pitzer parameter databank in the Aspen Physical Property System (see Physical Property Data).

Parameter Name	Symbol	No. of Elements	Default	MDS	Units
Cation-Anion Parameters					
GMPTB0	$\beta^{(0)}$	5	0	x	—
GMPTB1	$\beta^{(1)}$	5	0	x	—
GMPTB2	$\beta^{(2)}$	5	0	x	—
GMPTB3	$\beta^{(3)}$	5	0	x	—
GMPTC	C^{θ}	5	0	x	—
Cation-Cation Parameters					
GMPTTH	$\theta_{cc'}$	5	0	x	—
Anion-Anion Parameters					
GMPTTH	$\theta_{aa'}$	5	0	x	—
Cation1-Cation 2-Common Anion Parameters					
GMPTPS	$\Psi_{cc'a}$	1	0	x	—
Anion1-Anion2-Common Cation Parameters					
GMPTPS	$\Psi_{caa'}$	1	0	x	—
Molecule-Ion and Molecule-Molecule Parameters					
GMPTB0	$\beta^{(0)}$	5	0	x	—
GMPTB1	$\beta^{(1)}$	5	0	x	—
GMPTC	C^{θ}	5	0	x	—

Polynomial Activity Coefficient

This model represents activity coeficient as an empirical function of composition and temperature. It is used frequently in metallurgical applications where multiple liquid and solid solution phases can exist.

The equation is:

$$\ln \gamma_i = A_i + B_i x_i + C_i x_i^2 + D_i x_i^3 + E_i x_i^4$$

Where:

$$A_i \quad = \quad a_{i1}/T + a_{i2} + a_{i3}\ln(T)$$

$$B_i \quad = \quad b_{i1}/T + b_{i2} + b_{i3}\ln(T)$$

$$C_i \quad = \quad c_{i1}/T + c_{i2} + c_{i3}\ln(T)$$

$$D_i \quad = \quad d_{i1}/T + d_{i2} + d_{i3}\ln(T)$$

$$E_i \quad = \quad e_{i1}/T + e_{i2} + e_{i3}\ln(T)$$

For any component i, the value of the activity coefficient can be fixed:

$$\gamma_i = f_i$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
GMPLYP/1	a_{i1}	0	x	—	—	—
GMPLYP/2	a_{i2}	0	x	—	—	—
GMPLYP/3	a_{i3}	0	x	—	—	—
GMPLYP/4	b_{i1}	0	x	—	—	—
GMPLYP/5	b_{i2}	0	x	—	—	—
GMPLYP/6	b_{i3}	0	x	—	—	—
GMPLYP/7	c_{i1}	0	x	—	—	—
GMPLYP/8	c_{i2}	0	x	—	—	—
GMPLYP/9	c_{i3}	0	x	—	—	—
GMPLYP/10	d_{i1}	0	x	—	—	—
GMPLYP/11	d_{i2}	0	x	—	—	—
GMPLYP/12	d_{i3}	0	x	—	—	—
GMPLYP/13	e_{i1}	0	x	—	—	—
GMPLYP/14	e_{i2}	0	x	—	—	—
GMPLYP/15	e_{i3}	0	x	—	—	—
GMPLYO	f_i	—	x	—	—	—

Redlich-Kister

This model calculates activity coefficients. It is a polynomial in the difference between mole fractions in the mixture. It can be used for liquid and solid mixtures (mixed crystals).

The equation is:

$$\ln \gamma_i = \sum_{j=1}^{nc}\left[\sum_{n=1}^{5} x_j A_{n,ij}(x_i - x_j)^{n-2}(nx_i - x_j) - \tfrac{1}{2}\sum_{k=1}^{nc}\sum_{n=1}^{5} x_j x_k A_{n,jk}(x_j - x_k)^{n-2}\left[(2n-1)x_j - x_k\right]\right]$$

Where:

nc	=	Number of components
$A_{1,ij}$	=	$a_{ij}/T + b_{ij}$
$A_{2,ij}$	=	$c_{ij}/T + d_{ij}$
$A_{3,ij}$	=	$e_{ij}/T + f_{ij}$
$A_{4,ij}$	=	$g_{ij}/T + h_{ij}$
$A_{5,ij}$	=	$m_{ij}/T + n_{ij}$

For any component i, the value of the activity coefficient can be fixed:

$$\gamma_i = v_i$$

Parameter Name/ Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
GMRKTB/1	a_{ij}	0	X	—	—	—
GMRKTB/2	b_{ij}	0	X	—	—	—
GMRKTB/3	c_{ij}	0	X	—	—	—
GMRKTB/4	d_{ij}	0	X	—	—	—
GMRKTB/5	e_{ij}	0	X	—	—	—
GMRKTB/6	f_{ij}	0	X	—	—	—
GMRKTB/7	g_{ij}	0	X	—	—	—
GMRKTB/8	h_{ij}	0	X	—	—	—
GMRKTB/9	m_{ij}	0	X	—	—	—
GMRKTB/10	n_{ij}	0	X	—	—	—
GMRKTO	v_i	—	X	—	—	—

Scatchard-Hildebrand

The Scatchard-Hildebrand model calculates liquid activity coefficients. It is used in the CHAO-SEA property method and the GRAYSON property method.

The equation for the Scatchard-Hildebrand model is:

$$\ln \gamma_i = \frac{V_i^{*,l}}{RT} \sum_j \sum_k \varphi_j \varphi_k (A_{ji} - 1/2\, A_{jk})$$

Where:

$$A_{ij} \quad = \quad 2(\delta_i - \delta_j)^2$$

$$\varphi_i \quad = \quad \frac{x_i V_i^{*,l}}{V_m^l}$$

$$V_m^{*,L} \quad = \quad \sum_i x_i V_i^{*,l}$$

The Scatchard-Hildebrand model does not require binary parameters.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	x	5.0	2000.0	TEMPERATURE
DELTA	δ_i	—	x	10^3	10^5	SOLUPARAM
VLCVT1	$V_i^{*,CVT}$	—	x	0.0005	1.0	MOLE-VOLUME
GMSHVL	$V_i^{*,I}$	$V_i^{*,I} = V_i^{*,CVT}$ $5.7 + 3.0\left(\dfrac{298.15}{T_{ci}}\right)$	x	0.01	1.0	MOLE-VOLUME

Three-Suffix Margules

This model can be used to describe the excess properties of liquid and solid solutions. It does not find much use in chemical engineering applications, but is still widely used in metallurgical applications. Note that the binary parameters for this model do not have physical significance.

The equation is:

$$\ln \gamma_i = \tfrac{1}{2} \sum_j^{nc} (k_{ij} + k_{ji})x_j - \sum_j^{nc} \sum_l^{nc} k_{jl} x_j x_l + \sum_j^{nc} (k_{ij} - k_{ji})x_j (x_j/2 - x_i) \sum_j^{nc} \sum_l^{nc} (k_{jl} - k_{lj})x_l x_j^2$$

Where k_{ij} is a binary parameter:

$$k_{ij} = a_{ij}/T + b_{ij} + c_{ij} \ln(T)$$

For any component *i*, the value of the activity coefficient can be fixed:

$$\gamma_i = d_i$$

Parameter Name/ Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
GMMRGB/1	a_{ij}	0	x	—	—	TEMPERATURE
GMMRGB/2	b_{ij}	0	x	—	—	—
GMMRGB/3	c_{ij}	0	x	—	—	—
GMMRGO	d_i	—	x	—	—	—

References

M. Margules, "Über die Zusammensetzung der gesättigten Dämpfe von Mischungen," Sitzungsber. Akad. Wiss. Vienna, Vol. 104, (1895), p. 1293.

D.A. Gaskell, Introduction to Metallurgical Thermodyanics, 2nd ed., (New York: Hemisphere Publishing Corp., 1981), p. 360.

R.C. Reid, J.M. Prausnitz, and B.E. Poling, The Properties of Gases and Liquids, 4th ed., (New York: McGraw-Hill, 1987).

UNIFAC

The UNIFAC model calculates liquid activity coefficients for the following property methods: UNIFAC, UNIF-HOC, and UNIF-LL. Because the UNIFAC model is a group-contribution model, it is predictive. All published group parameters and group binary parameters are stored in the Aspen Physical Property System.

The equation for the original UNIFAC liquid activity coefficient model is made up of a combinatorial and residual term:

$$\ln \gamma = \ln \gamma_i^c + \ln \gamma_i^r$$

$$\ln \gamma_i^c = \ln\left(\frac{\Phi_i}{x_i}\right) + 1 - \frac{\Phi_i}{x_i} - \frac{Z}{2}\left[\ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i}\right]$$

Where the molecular volume and surface fractions are:

$$\Phi_i = \frac{x_i r_i}{\sum_j^{nc} x_j r_j} \qquad \theta_i = \frac{x_i \frac{z}{2} q_i}{\sum_j^{nc} x_j \frac{z}{2} q_j}$$
and

Where nc is the number of components in the mixture. The coordination number z is set to 10. The parameters ri and qi are calculated from the group volume and area parameters:

$$r_i = \sum_k^{ng} v_{ki} R_k \qquad q_i = \sum_k^{ng} v_{ki} Q_k$$
and

Where v_{ki} is the number of groups of type *k* in molecule *i*, and *ng* is the number of groups in the mixture.

The residual term is:

$$\ln \gamma_i^r = \sum_k^{ng} \nu_{ki} \left[\ln \Gamma_k - \ln \Gamma_k^i \right]$$

Γ_k is the activity coefficient of a group at mixture composition, and Γ_k^i is the activity coefficient of group k in a mixture of groups corresponding to pure i. The parameters Γ_k and Γ_k^i are defined by:

$$\ln \Gamma_k = Q_k \left(1 - \ln \sum_m^{ng} \theta_m \tau_{mk} - \sum_m^{ng} \left(\frac{\theta_m \tau_{km}}{\sum_n^{ng} \theta_n \tau_{nm}} \right) \right)$$

With:

$$\theta_k = \frac{X_k \frac{z}{2} Q_k}{\sum_m^{ng} X_m \frac{z}{2} Q_m}$$

And:

$$\tau_{mn} = e^{-b_{mn}/T}$$

The parameter X_k is the group mole fraction of group k in the liquid:

$$X_k = \frac{\sum_j^{nc} \nu_{kj} x_j}{\sum_j^{nc} \sum_m^{ng} \nu_{mj} x_j}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
UFGRP	$(\nu_{ki}\ \nu_{mi} ...)$	—	—	—	—	—
GMUFQ	Q_k	—	—	—	—	—
GMUFR	R_k	—	—	—	—	—
GMUFB	b_{kn}	—	—	—	—	TEMPERATURE

The parameter UFGRP stores the UNIFAC functional group number and number of occurrences of each group. UFGRP is stored in the Aspen Physical Property System pure component databank for most components. For nondatabank components, enter UFGRP on the Properties Molecular Structure Functional

Group sheet. See Physical Property Data, Chapter 3, for a list of the UNIFAC functional groups.

References

Aa. Fredenslund, J. Gmehling and P. Rasmussen, "Vapor-Liquid Equilibria using UNIFAC," (Amsterdam: Elsevier, 1977).

Aa. Fredenslund, R.L. Jones and J.M. Prausnitz, AIChE J., Vol. 21, (1975), p. 1086.

H.K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, "Vapor-Liquid Equilibria by UNIFAC Group Contribution. 5 Revision and Extension", Ind. Eng. Chem. Res., Vol. 30, (1991), pp. 2352-2355.

UNIFAC (Dortmund Modified)

The UNIFAC modification by Gmehling and coworkers (Weidlich and Gmehling, 1987; Gmehling et al., 1993), is slightly different in the combinatorial part. It is otherwise unchanged compared to the original UNIFAC:

$$\ln \gamma_i^c = \ln\left(\frac{\Phi_i'}{x_i}\right) + 1 - \frac{\Phi_i}{x_i} - \frac{z}{2} q_i\left(\ln\frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i}\right)$$

With:

$$\frac{\Phi_i'}{x_i} = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}}$$

The temperature dependency of the interaction parameters is:

$$a_{mn} = a_{mn,1} + a_{mn,2}T + a_{mn,3}T^2$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
UFGRPD	$(k\nu_{ki}\, m\nu_{mi}\,...)$	—	—	—	—	—
GMUFDQ	Q_k	—	—	—	—	—
GMUFDR	R_k	—	—	—	—	—
UNIFDM/1	$a_{mn,1}$	0	—	—	—	TEMPERATURE
UNIFDM/2	$a_{mn,2}$	0	—	—	—	TEMPERATURE
UNIFDM/3	$a_{mn,3}$	0	—	—	—	TEMPERATURE

The parameter UFGRPD stores the group number and the number of occurrences of each group. UFGRPD is stored in the Aspen Physical Property System pure component databank. For nondatabank components, enter UFGRPD on the Properties Molecular Structure Functional Group sheet. See Physical Property Data, Chapter 3, for a list of the Dortmund modified UNIFAC functional groups.

U. Weidlich and J. Gmehling, "A Modified UNIFAC Model 1.

Prediction of VLE, h^E and γ^∞," Ind. Eng. Chem. Res., Vol. 26, (1987), pp. 1372–1381.

J. Gmehling, J. Li, and M. Schiller, "A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties," Ind. Eng. Chem. Res., Vol. 32, (1993), pp. 178–193.

UNIFAC (Lyngby Modified)

The equations for the "temperature-dependent UNIFAC" (Larsen et al., 1987) are similar to the original UNIFAC:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r,$$

$$\ln \gamma_i^c = \ln\left(\frac{\omega_i}{x_i}\right) + 1 - \frac{\omega_i}{x_i}$$

Volume fractions are modified:

$$\omega_i = \frac{x_i r_i^{2/3}}{\sum_j^{nc} x_j r_j^{2/3}}$$

With:

$$r_i = \sum_k^{ng} \nu_{ki} R_k$$

$$\ln \gamma_i^r = \sum_k^{ng} \nu_{ki}\left(\ln \Gamma_k - \ln \Gamma_k^i\right)$$

Where Γ_k and Γ_k^i have the same meaning as in the original UNIFAC, but defined as:

$$\ln \Gamma_k = \frac{z}{2} Q_k \left[1 - \ln\left(\sum_m^{ng} \theta_m \tau_{mk}\right) + \sum_m^{ng}\left(\frac{\theta_m \tau_{km}}{\sum_n^{ng} \theta_n \tau_{nm}}\right)\right]$$

With:

$$\theta_k = \frac{X_k \frac{z}{2} Q_k}{\sum_m^{ng} X_m \frac{z}{2} Q_m}$$

$$\tau_{mn} = e^{-a_{mn}/T}$$

The temperature dependency of a is described by a function instead of a constant:

$$a_{mn} = a_{mn,1} + a_{mn,2}(T - 298.15) + a_{mn,3}\left(T \ln \frac{298.15}{T} + T - 298.15\right)$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
UFGRPL	$(\nu_{ki}\ \nu_{mi}\ ...)$	—	—	—	—	—
GMUFLQ	Q_k	—	—	—	—	—
GMUFLR	R_k	—	—	—	—	—
UNIFLB/1	$a_{mn,1}$	0	—	—	—	TEMPERATURE
UNIFLB/2	$a_{mn,2}$	0	—	—	—	TEMPERATURE
UNIFLB/3	$a_{mn,3}$	0	—	—	—	TEMPERATURE

The parameter UFGRPL stores the modified UNIFAC functional group number and the number of occurrences of each group. UFGRPL is stored in the Aspen Physical Property System pure component databank. For nondatabank components, enter UFGRP on the Properties Molec-Struct.Func Group form. See Physical Property Data, Chapter 3, for a list of the Larsen modified UNIFAC functional groups.

B. Larsen, P. Rasmussen, and Aa. Fredenslund, "A Modified UNIFAC Group-Contribution Model for Prediction of Phase Equilibria and Heats of Mixing," Ind. Eng. Chem. Res., Vol. 26, (1987), pp. 2274 – 2286.

UNIQUAC

The UNIQUAC model calculates liquid activity coefficients for these property methods: UNIQUAC, UNIQ-2, UNIQ-HOC, UNIQ-NTH, and UNIQ-RK. It is recommended for highly non-ideal chemical systems, and can be used for VLE and LLE applications. This model can also be used in the advanced equations of state mixing rules, such as Wong-Sandler and MHV2.

The equation for the UNIQUAC model is:

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} - q_i' \ln t_i' - q_i' \sum_j \theta_j' \tau_{ij} \bigg/ t_j' + l_i + q_i' - \frac{\Phi_i}{x_i} \sum_j x_j l_j$$

Where:

$$\theta_i \quad = \quad q_i x_i \bigg/ q_T \ ; \ q_T = \sum_k q_k x_k$$

$$\theta_i' \quad = \quad q_i' x_i \bigg/ q_T' \ ; \ q_T' = \sum_k q_k' x_k$$

$$\Phi_i \quad = \quad \Phi_i = r_i x_i \Big/ r_T \; ; \; r_T = \sum_k r_k x_k$$

$$l_i \quad = \quad \frac{z}{2}(r_i - q_i) + 1 - r_i$$

$$t_i' \quad = \quad \sum_k \theta_k' \tau_{ki}$$

$$\tau_{ij} \quad = \quad \exp(a_{ij} + b_{ij}/T + C_{ij} \ln T + d_{ij} T$$

$$z \quad = \quad 10$$

$$a_{ij} \quad = \quad a_{ji}$$

$$b_{ij} \quad = \quad b_{ji}$$

$$c_{ij} \quad = \quad c_{ji}$$

$$d_{ij} \quad = \quad d_{ji}$$

The binary parameters a_{ij}, b_{ij}, c_{ij}, and d_{ij} can be determined from VLE and/or LLE data regression. The Aspen Physical Property System has a large number of built-in parameters for the UNIQUAC model. The binary parameters have been regressed using VLE and LLE data from the Dortmund Databank. The binary parameters for VLE applications were regressed using the ideal gas, Redlich-Kwong, and Hayden-O'Connell equations of state. See Physical Property Data, Chapter 1, for details.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
GMUQR	r_i	—	x	—	—	—
GMUQQ	q_i	—	x	—	—	—
GMUQQ1	q_i'	q	x	—	—	—
UNIQ/1	a_{ij}	0	x	-50.0	50.0	—
UNIQ/2	b_{ij}	0	x	-15000.0	15000.0	TEMPERATURE
UNIQ/3	c_{ij}	0	x	—	—	TEMPERATURE
UNIQ/4	d_{ij}	0	x	—	—	TEMPERATURE

Absolute temperature units are assumed.

References

D.S. Abrams and J.M. Prausnitz, "Statistical Thermodynamics of liquid mixtures: A new expression for the Excess Gibbs Energy of

Partly or Completely Miscible Systems," AIChE J., Vol. 21, (1975), p. 116.

A. Bondi, "Physical Properties of Molecular Crystals, Liquids and Gases," (New York: Wiley, 1960).

Simonetty, Yee and Tassios, "Prediction and Correlation of LLE," Ind. Eng. Chem., Process Des. Dev., Vol. 21, (1982), p. 174.

Van Laar

The Van Laar model (Van Laar 1910) calculates liquid activity coefficients for the property methods: VANLAAR, VANL-2, VANL-HOC, VANL-NTH, and VANL-RK. It can be used for highly nonideal systems.

$$\ln \gamma_i = A_i (1 - z_i)^2 \left[1 + C_i z_i (z_i - \tfrac{2}{3}) + 2 z_i \left(A_i B_i / |A_i B_i| - 1 \right) \right]$$

Where:

z_i	$=$	$\dfrac{\|A_i\| x_i}{\|A_i\| x_i + \|B_i\|(1 - x_i)}$
A_i	$=$	$\sum_j x_j A_{ij} / (1 - x_i)$
B_i	$=$	$\sum_j x_j A_{ji} / (1 - x_i)$
C_i	$=$	$\sum_j x_j C_{ij} / (1 - x_i)$
A_{ij}	$=$	$a_{ij} + b_{ij} / T$
C_{ij}	$=$	$c_{ij} + d_{ij} / T$
C_{ij}	$=$	C_{ji}
A_{ii}	$=$	$B_{ii} = C_{ii} = 0$
a_{ij}	$=$	a_{ji}
b_{ij}	$=$	b_{ji}

Parameters Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
VANL/1	a_{ij}	0	x	-50.0	50.0	—
VANL/2	b_{ij}	0	x	-15000.0	15000.0	TEMPERATURE
VANL/3	c_{ij}	0	x	-50.0	50.0	—
VANL/4	d_{ij}	0	x	-15000.0	15000.0	TEMPERATURE

References

J.J. Van Laar, "The Vapor Pressure of Binary Mixtures," Z. Phys. Chem., Vol. 72, (1910), p. 723.

R.C. Reid, J.M. Prausnitz, and B.E. Poling, The Properties of Gases and Liquids, 4th ed. (New York: McGraw-Hill, 1987).

Wagner Interaction Parameter

The Wagner Interaction Parameter model calculates activity coefficients. This model is used for dilute solutions in metallurgical applications.

The relative activity coefficient with respect to the reference activity coefficient of a solute i (in a mixture of solutes i, j, and l and solvent A) is:

$$\ln\left(\gamma_i/\gamma_i^{ref}\right) = \ln\gamma_A + \sum_{j=1}^{nc} k_{ij}x_i \quad j \neq A$$

Where:

$$\ln\gamma_A = -\tfrac{1}{2}\sum_j^{nc}\sum_l^{nc} k_{jl}x_j x_l \quad j \text{ and } l \neq A$$

The parameter γ_i^{ref} is the reference activity coefficient of solute i:

$$\ln\gamma_i^{ref} = a_i/T + b_i + c_i\ln(T)$$

k_{ij} is a binary parameter:

$$k_{ij} = d_{ij}/T + e_{ij} + f_{ij}\ln(T)$$

For any component i, the value of the activity coefficient can be fixed:

$$\gamma_i = g_i$$

This model is recommended for dilute solutions.

Parameter Name/ Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
GMWIPR/1	a_i	0	x	—	—	TEMPERATURE
GMWIPR/2	b_i	0	x	—	—	—
GMWIPR/3	c_i	0	x	—	—	—
GMWIPB/1	d_{ij}	0	x	—	—	TEMPERATURE
GMWIPB/2	e_{ij}	0	x	—	—	—
GMWIPB/3	f_{ij}	0	x	—	—	—
GMWIPO	g_i	—	x	—	—	—
GMWIPS		—	0	x	—	—	—

GMWIPS is used to identify the solvent component. You must set GMWIPS to 1.0 for the solvent component. This model allows only one solvent.

References

A.D. Pelton and C. W. Ball, "A Modified Interaction Parameter Formalism for Non-Dilute Solutions," Metallurgical Transactions A, Vol. 17A, (July 1986), p. 1211.

Wilson

The Wilson model calculates liquid activity coefficients for the property methods: WILSON, WILS2, WILS-HOC, WILS-NTH, WILS-RK, and WILS-HF. It is recommended for highly nonideal systems, especially alcohol-water systems. It can also be used in the advanced equation-of-state mixing rules, such as Wong-Sandler and MHV2. This model cannot be used for liquid-liquid equilibrium calculations.

The equation for the Wilson model is:

$$\ln \gamma_i = 1 - \ln\left(\sum_j A_{ij} x_j\right) - \sum_j \frac{A_{ji} x_j}{\sum_k A_{jk} x_k}$$

Where:

$\ln A_{ij}$	$=$	$a_{ij} + b_{ij}/T + c_{ij} \ln T + d_{ij}T$
a_{ij}	$=$	a_{ji}
b_{ij}	$=$	b_{ji}
c_{ij}	$=$	c_{ji}
d_{ij}	$=$	d_{ji}

The binary parameters a_{ij}, b_{ij}, c_{ij}, and d_{ij} must be determined from VLE data regression. The Aspen Physical Property System has a large number of built-in binary parameters for the Wilson model. The binary parameters have been regressed using VLE data from the Dortmund Databank. The binary parameters were regressed using the ideal gas, Redlich-Kwong, and Hayden-O'Connell equations of state. See Physical Property Data, Chapter 1, for details.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
WILSON/1	a_{ij}	0	x	-50.0	50.0	—
WILSON/2	b_{ij}	0	x	-15000.0	15000.0	TEMPERATURE
WILSON/3	c_{ij}	0	x	——	—	TEMPERATURE
WILSON/4	d_{ij}	0	x	—	—	TEMPERATURE

Absolute temperature units are assumed.

References

G.M. Wilson, J. Am. Chem. Soc., Vol. 86, (1964), p. 127.

Wilson Model with Liquid Molar Volume

This Wilson model calculates liquid activity coefficients using the original formulation of Wilson (Wilson 1964) except that liquid molar volume is calculated at system temperature, instead of at 25°C. It is recommended for highly nonideal systems, especially alcohol-water systems. It can be used in any activity coefficient property method or in the advanced equation-of-state mixing rules, such as Wong-Sandler and MHV2. This model cannot be used for liquid-liquid equilibrium calculations.

The equation for the Wilson model is:

$$\ln \gamma_i = 1 - \ln\left(\sum_j A_{ij} x_j\right) - \sum_j \frac{A_{ji} x_j}{\sum_k A_{jk} x_k}$$

Where:

$$\ln A_{ij} \quad = \quad \ln \frac{V_j}{V_i} + \frac{b_{ij}}{T}$$

$$b_{ij} \quad = \quad b_{ji}$$

V_i and V_j are liquid molar volume at the system temperature calculated using the Rackett model.

The binary parameters b_{ij} and b_{ji} must be determined from VLE data regression. There are no built-in binary parameters for this model.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
WSNVOL/1	b_{ij}	0	x	-15000.0	15000.0	TEMPERATURE

Absolute temperature units are assumed.

Pure component parameters for the Rackett model are also required.

G.M. Wilson, *J. Am. Chem. Soc.,* Vol. 86, (1964), p. 127.

Vapor Pressure and Liquid Fugacity Models

The Aspen Physical Property System has 4 built-in vapor pressure and liquid fugacity models. This section describes the vapor pressure and liquid fugacity models available.

Model	Type
Extended Antoine/Wagner/IK-CAPE	Vapor pressure
Chao-Seader	Fugacity
Grayson-Streed	Fugacity
Kent-Eisenberg	Fugacity
Maxwell-Bonnell	Vapor pressure

Extended Antoine/Wagner/IK-CAPE

The vapor pressure of a liquid can be calculated using the extended Antoine equation, the Wagner equation, or the IK-CAPE equation.

Extended Antoine Equation

Many parameters are available for the extended Antoine equation from the Aspen Physical Property System pure component databank. This equation is used whenever the parameter PLXANT is available.

The equation for the extended Antoine vapor pressure model is:

$$\ln p_i^{*,l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln T + C_{6i}\,T^{C_{7i}} \ \text{ for } C_{8i} \le C_{9i}$$

Extrapolation of $\ln p_i^{*,l}$ versus 1/T occurs outside of temperature bounds.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
PLXANT/1	C_{1i}	—	x	—	—	PRESSURE, TEMPERATURE
PLXANT/2	C_{2i}	—	x	—	—	TEMPERATURE
PLXANT/3, . . . , 7	$C_{3i},...,C_{7i}$	0	x	—	—	TEMPERATURE
PLXANT/8	C_{8i}	0	x	—	—	TEMPERATURE
PLXANT/9	C_{9i}	1000	x	—	—	TEMPERATURE

If elements 5, 6, or 7 are non-zero, absolute temperature units are assumed for elements 1 through 7.

Wagner Vapor Pressure Equation

The Wagner vapor pressure equation is the best equation for correlation. However, its results are sensitive to the values of Tc

and pc. The equation is used if the parameter WAGNER is available:

$$\ln p_{ri}^{*,l} = \left(C_{1i}\left(1 - T_{ri}\right) + C_{2i}\left(1 - T_{ri}\right)^{1.5} + C_{3i}\left(1 - T_{ri}\right)^{3} + C_{4i}\left(1 - T_{ri}\right)^{6} \right) / T_{ri}$$

Where:

$$T_{ri} = T / T_{ci}$$

$$p_{ri}^{*,l} = p_{i}^{*,l} / p_{ci}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
WAGNER/1	C_{1i}	—	x	—	—	—
WAGNER/2	C_{2i}	0	x	—	—	—
WAGNER/3	C_{3i}	0	x	—	—	—
WAGNER/4	C_{4i}	0	x	—	—	—
TC	T_{ci}	—	—	—	—	TEMPERATURE
PC	p_{ci}	—	—	—	—	PRESSURE

IK-CAPE Vapor Pressure Equation

The IK-CAPE model is a polynomial equation. If the parameter PLPO is available, the Aspen Physical Property System uses the IK-CAPE vapor pressure equation:

$$\ln p_{i}^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^{2} + C_{4i}T^{3} + C_{5i}T^{4} + C_{6i}T^{5} + C_{7i}T^{6} + C_{8i}T^{7} + C_{9i}T^{8} + C_{10i}T^{9}$$

for $C_{11i} \leq T \leq C_{12i}$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
PLPO/1	C_{1i}	—	X	—	—	PRESSURE TEMPERATURE
PLPO/2,…,10	C_{10i}	0	X	—	—	TEMPERATURE
PLPO/11	C_{11i}	0	X	—	—	TEMPERATURE
PLPO/12	C_{12i}	1000	X	—	—	TEMPERATURE

References

Reid, Prausnitz, and Poling, The Properties of Gases and Liquids, 4th ed., (New York: McGraw-Hill, 1987).

Harlacher and Braun, "A Four-Parameter Extension of the Theorem of Corresponding States," Ind. Eng. Chem. Process Des. Dev., Vol. 9, (1970), p. 479.

W. Wagner, Cryogenics, Vol. 13, (1973), pp. 470-482.

Chao-Seader

The Chao-Seader model calculates pure component fugacity coefficient, for liquids. It is used in the CHAO-SEA property method. This is an empirical model with the Curl-Pitzer form. The general form of the model is:

$$\ln \varphi_i^{*,l} = \ln \nu_i^{(0)} + \omega_i \ln \nu_i^{(1)}$$

Where:

$$\nu_i^{(0)}, \nu_i^{(1)} \quad = \quad fcn\left(T, T_{ci}, p, p_{ci}\right)$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
PC	p_{ci}	—	—	10^5	10^8	PRESSURE
OMEGA	ω_i	—	—	-0.5	2.0	—

References

K.C. Chao and J.D. Seader, "A General Correlation of Vapor-Liquid Equilibria in Hydrocarbon Mixtures," AIChE J., Vol. 7, (1961), p. 598.

Grayson-Streed

The Grayson-Streed model calculates pure component fugacity coefficients for liquids, and is used in the GRAYSON/GRAYSON2 property methods. It is an empirical model with the Curl-Pitzer form. The general form of the model is:

$$\ln \varphi_i^{*,l} = \ln \nu_i^{(0)} + \omega_i \ln \nu_i^{(1)}$$

Where:

$$\nu_i^{(0)}, \nu_i^{(1)} = fcn\left(T, T_{ci}, p, p_{ci}\right)$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
PC	p_{ci}	—	—	10^5	10^8	PRESSURE
OMEGA	ω_i	—	—	-0.5	2.0	—

References

H.G. Grayson and C.W. Streed, Paper 20-PO7, Sixth World Petroleum Conference, Frankfurt, June 1963.

Kent-Eisenberg

The Kent-Eisenberg model calculates liquid mixture component fugacity coefficients and liquid enthalpy for the AMINES property method.

The chemical equilibria in $H_2S + CO_2 + amine$ systems are described using these chemical reactions:

$$RR'NH_2^+ \quad \overset{K_1}{=} \quad H^+ + RR'NH$$

$$RR'NCOO^- + H_2O \quad \overset{K_2}{=} \quad RR'NH + HCO_3^-$$

$$H_2O + CO_2 \quad \overset{K_3}{=} \quad H^+ + HCO_3^-$$

$$H_2O \quad \overset{K_4}{=} \quad H^+ + OH^-$$

$$HCO_3^- \quad \overset{K_5}{=} \quad H^+ + CO_3^{2-}$$

$$H_2S \quad \overset{K_6}{=} \quad H^+ + HS^{2-}$$

$$HS^- \quad \overset{K_7}{=} \quad H^+ + S^{2-}$$
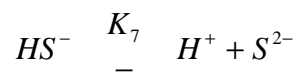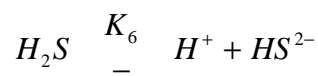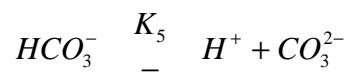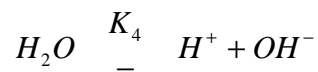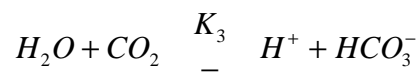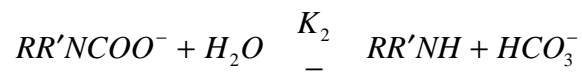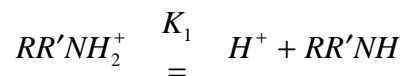
Where:

R' =   Alcohol substituted alkyl groups

The equilibrium constants are given by:

$$\ln K_i = A_{1i} + A_{2i}/T + A_{3i}/T^2 + A_{4i}/T^3 + A_{5i}/T^4$$

The chemical equilibrium equations are solved simultaneously with the balance equations. This obtains the mole fractions of free H_2S and CO_2 in solution. The equilibrium partial pressures of H_2S and CO_2 are related to the respective free concentrations by Henry's constants:

$$\ln H_i = B_{1i} + B_{2i}/T$$

The apparent fugacities and partial molar enthalpies, Gibbs energies and entropies of H_2S and CO_2 are calculated by standard thermodynamic relationships. The chemical reactions are always considered.

The values of the coefficients for the seven equilibrium constants $(A_{1i}, ..., A_{5i})$ and for the two Henry's constants B_{1i} and B_{2i} are built into the Aspen Physical Property System. The coefficients for the equilibrium constants were determined by regression. All available

data for the four amines were used: monoethanolamine, diethanolamine, disopropanolamine and diglycolamine.

You are not required to enter any parameters for this model.

References

R.L. Kent and B. Eisenberg, Hydrocarbon Processing, (February 1976), pp. 87-92.

Maxwell-Bonnell   The Maxwell-Bonnell model calculates vapor pressure using the Maxwell-Bonnell vapor pressure correlation for all hydrocarbon pseudo-components as a function of temperature. This is an empirical correlation based on API procedure 5A1.15, 5A1.13. This model is used in property method MXBONNEL for calculating vapor pressure and liquid fugacity coefficients (K-values).

References

API procedure 5A1.15 and 5A1.13.

Heat of Vaporization Model

The Aspen Physical Property System uses two models to calculate pure component heat of vaporization: the Watson/DIPPR/IK-CAPE model and the Clausius-Clapeyron model. For the Watson/DIPPR/IK-CAPE model, the DIPPR equation is the primary equation used for all components. The Watson equation is used in PCES. The IK-CAPE equation is a polynomial equation, and is used when the parameter DHVLPO is available.

DIPPR Equation   The equation for the DIPPR heat of vaporization model is:

$$\Delta_{vap} H_i^* = C_{1i} \left(1 - T_{ri}\right)^{\left(C_{2i} + C_{3i} T_{ri} + C_{4i} T_{ri}^2 + C_{5i} T_{ri}^3\right)} \text{ for } C_{6i} \leq T \leq C_{7i}$$

Where:

$$T_{ri} = T / T_{ci}$$

Extrapolation of $\Delta_{vap} H_i^*$ versus T occurs outside of temperature bounds.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
DHVLDP/1	C_{1i}	—	x	—	—	MOLE-ENTHALPY
DHVLDP/2, . , 5	$C_{2i},...,C_{5i}$	0	x	—	—	—
DHVLDP/6	C_{6i}	0	x	—	—	TEMPERATURE
DHVLDP/7	C_{7i}	1000	x	—	—	TEMPERATURE
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE

Watson Equation

The equation for the Watson model is:

$$\Delta_{vap}H_i^*(T) = \Delta_{vap}H_i^*(T_1)\left(\frac{1-T/T_{ci}}{1-T_1/T_{ci}}\right)^{a_i+b_i(1-T/T_{ci})} \quad \text{for } T > T_{\min}$$

Where:

$$\Delta_{vap}H_i^*(T_1) \quad = \quad T_1$$

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	5.0	2000.0	TEMPERATURE
DHVLWT/1	$\Delta_{vap}H_i^*(T_1)$	—	5×10^4	5×10^8	MOLE-ENTHALPY
DHVLWT/2	T_1	—	4.0	3500.0	TEMPERATURE
DHVLWT/3	a_i	0.38	-2.0	2.0	—
DHVLWT/4	b_i	0	-2.0	2.0	—
DHVLWT/5	$T_{\min}$	0	0.0	1500.0	TEMPERATURE

IK-CAPE Equation

The equation for the IK-CAPE model is:

$$\Delta_{vap}H_i^*(T) = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

for $C_{11i} \leq T \leq C_{12i}$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
DHVLPO/1	C_{1i}	—	X	—	—	MOLE-ENTHALPY
DHVLPO/2,…,10	C_{10i}	0	X	—	—	MOLE-ENTHALPY TEMPERATURE
DHVLPO/11	C_{11i}	0	X	—	—	TEMPERATURE
DHVLPO/12	C_{12i}	1000	X	—	—	TEMPERATURE

Clausius-Clapeyron Equation

The Aspen Physical Property System can calculate heat of vaporization using the Clausius-Clapeyron equation:

$$\Delta_{vap}H_i^* = \frac{d\,p_i^{*,l}}{dT}T\left(V_i^{*,v} - V_i^{*,l}\right)$$

Where:

$\dfrac{d\,p_i^{*,l}}{dT}$ = Slope of the vapor pressure curve calculated from the Extended Antoine equation

$V_i^{*,v}$ = Vapor molar volume calculated from the Redlich-Kwong equation-of-state

$V_i^{*,l}$ = Liquid molar volume calculated from the Rackett equation

For parameter requirements, see Extended Antoine/Wagner, the Rackett model, and Redlich-Kwong., all in this chapter.

Molar Volume and Density Models

The Aspen Physical Property System has nine built-in molar volume and density models available. This section describes the molar volume and density models.

Model	Type
API Liquid Volume	Liquid volume
Brelvi-O'Connell	Partial molar liquid volume of gases
Clarke Aqueous Electrolyte Volume	Liquid volume
Costald Liquid Volume	Liquid volume
Debije-Hückel Volume	Electrolyte liquid volume
Rackett/DIPPR/IK-CAPE Pure Component Liquid Volume	Liquid volume/liquid density
Rackett Mixture Liquid Volume	Liquid volume
Modified Rackett	Liquid volume
Aspen/IK-CAPE Solids Volume	Solid volume

API Liquid Volume

This model calculates liquid molar volume for a mixture, using the API procedure and the Rackett model. Ideal mixing is assumed:

$$V_m^l = x_p V_p^l + x_r V_r^l$$

Where:

x_p = Mole fraction of pseudocomponents

x_r = Mole fraction of real components

For pseudocomponents, the API procedure is used:

$$V_p^l = fcn\left(T, T_b, API\right)$$

Where:

fcn = A correlation based on API Figure 6A3.5 *(API Technical Data Book, Petroleum Refining, 4th edition)*

For real components, the mixture Rackett model is used:

$$V_r^l = \frac{RT_c Z^{RA\left[1+\left(1-T_r\right)^{2/7}\right]}}{p_c}$$

See the Rackett model for descriptions.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TB	T_b	—	—	4.0	2000.0	TEMPERATURE
API	API	—	—	-60.0	500.0	—
TC	T_c	—	—	5.0	2000.0	TEMPERATURE
PC	p_c	—	—	10^5	10^8	PRESSURE
RKTZRA	$Z\frac{RA}{r}$	ZC	—	0.1	0.5	—

Brelvi-O'Connell

The Brelvi-O'Connell model calculates partial molar volume of a supercritical component i at infinite dilution in pure solvent A. Partial molar volume at infinite dilution is required to compute the effect of pressure on Henry's constant. (See Henry's Constant.)

The general form of the Brelvi-O'Connell model is:

$$V_{iA}^{\infty} = fcn\left(V_i^{BO}, V_A^{BO}, V_A^{*l}\right)$$

Where:

i = Solute or dissolved-gas component

A = Solvent component

The liquid molar volume of solvent is obtained from the Rackett model:

$$V_i^{*,l} = \frac{RT_{cA}Z_A^{RA\left[1+\left(1-T_{rA}\right)^{2/7}\right]}}{p_{cA}}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{cA}	—	—	5.0	2000.0	TEMPERATURE
PC	p_{cA}	—	—	105	108	PRESSURE
RKTZRA	Z_A^{RA}	ZC	x	0.1	1.0	—
VLBROC/1	V_i^{BO}	VC	x	-1.0	1.0	MOLE-VOLUME
VLBROC/2	—	0	x	-0.1	0.1	TEMPERATURE

References

S.W. Brelvi and J.P. O'Connell, AIChE J., Vol. 18, (1972), p. 1239.

S.W. Brelvi and J.P. O'Connell, AIChE J., Vol. 21, (1975), p. 157.

Clarke Aqueous Electrolyte Volume

The Clarke model calculates liquid molar volume for electrolytes solutions. The model is applicable to mixed solvents and is based on:

- Amagat's law (equation 1)

- The relationship between the partial molar volume of an electrolyte and its mole fraction in the solvent (equation 2)

All quantities are expressed in terms of apparent components.

Apparent Component Approach

Amagat's law is:

$$V_m^l = \sum_i x_i V_i \tag{1}$$

For water and molecular solutes, $V_i = V_i^*$ and is computed from the Rackett equation. If water is the only molecular component, the ASME steam table is used to compute V_i^* for water.

For electrolytes:

$$V_{ca} = V_{ca}^\infty + A_{ca} \frac{\sqrt{x_{ca}}}{1 + \sqrt{x_{ca}}} \tag{2}$$

Where:

x_{ca} =   Apparent electrolyte mole fraction

The mole fractions x_{ca} are reconstituted arbitrarily from the true ionic concentrations, even if you use the apparent component approach. This technique is explained in Electrolyte Calculation, Chapter 5.

The result is that electrolytes are generated from all possible combinations of ions in solution. For example: given an aqueous solution of Ca^{2+}, Na^+, SO_4^{2-}, Cl^- four electrolytes are found: $CaCl_2$, Na_2SO_4, $CaSO_4$ and NaCl. The Clarke parameters of all four electrolytes are used. You can rely on the default, which calculates the Clarke parameters from ionic parameters. Otherwise, you must enter parameters for any electrolytes that may not exist in the components list. If you do not want to use the default, the first step in using the Clarke model is to enter any needed component ID's for electrolytes not in the components list.

The mole fractions of apparent electrolytes used in the calculation are all nonzero, but are arbitrary values. For a given ionic solution, the Clarke model always yields the same volume, independent of the mole fractions of the electrolytes. Constraints between the Clarke parameters result:

$$V_{CaCl_2}^{\infty} + V_{Na_2SO_4}^{\infty} = V_{CaSO_4}^{\infty} + 2V_{NaCl}^{\infty}$$

A similar equation exists for A_{ca} You can consider these constraints in simple parameter input and in data regression.

True Component Approach

The true molar volume is obtained from the apparent molar volume:

$$V_m^{l,t} = V_m^{l,a} \frac{n^a}{n^t}$$

Where:

$V_m^{l,t}$	=	Liquid volume per number of true species
$V_m^{l,a}$	=	Liquid volume per number of apparent species, V_m^l of equation 1
n^a	=	Number of apparent species
n^t	=	Number of true species

The apparent molar volume is calculated as explained in the preceding subsection.

Temperature Dependence

The temperature dependence of the molar volume of the solution is approximately equal to the temperature dependence of the molar volume of the solvent mixture:

$$V_m^l(T) = V_m^l(298K) \frac{\sum_B x_B V_B^{*,l}(T)}{\sum_B x_B V_B^{*,l}(298K)}$$

Where:

B	=	Any solvent

Parameter Name/Element	Applicable Components	Symbol	Default	Units
VLCLK/1	Cation-Anion	V_{ca}^{∞}	†	MOLE-VOLUME
VLCLK/2	Cation-Anion	A_{ca}	0.020	MOLE-VOLUME

† If VLCLK/1 is missing, it is calculated based on VLBROC and CHARGE. If VLBROC is missing, the default value of $-0.12x10^{-2}$ is used.

COSTALD Liquid Volume   The equation for the COSTALD liquid volume model is:

$$V_m^{sat} = V_m^{CTD} V_m^{R,0} \left(1 - \omega V_m^{R,\delta}\right)$$

Where:

$V_m^{R,0}$ and $V_m^{R,\delta}$ are functions or T_r for $0.25 < T_r \leq 0.95$

For $0.95 < T_r \leq 1.0$, there is a linear interpolation between the liquid density at

$T_r = 0.95$ and the vapor density at $T_r = 1.05$. This model can be used to calculate saturated and compressed liquid molar volume. The compresed liquid molar volume is calculated using the Tait equation.

Mixing Rules:

$$V_m^{CTD} = \frac{1}{4}\left[\left(\sum_i x_i V_i^{*,CTD} + 3\sum_i x_i (V_i^{*,CTD})^{2/3}\right)\left(\sum_i x_i (V_i^{*,CTD})^{1/3}\right)\right]$$

$$V_m^{CTD} T_c = \sum_i \sum_j x_i x_j V_{ij}^{CTD} T_{cij}$$

$$\omega = \sum_i x_i \omega_i$$

Where:

$$V_{ij}^{CTD} T_{cij} = \left(V_i^{*,CTD} T_{ci} V_j^{*,CTD} T_{cj}\right)^{\frac{1}{2}}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
VSTCTD	$V_i^{*,CTD}$	VC	X	0.001	3.5	MOLE-VOLUME
OMGCTD	ω_i	OMEGA	X	-0.5	2.0	—

References

R.W. Hankinson and G.H. Thomson, AIChE J., Vol. 25, (1979), p. 653.

G.H. Thomson, K.R. Brobst, and R.W. Hankinson, AIChE J., Vol. 28, (1982), p. 4, p. 671.

Debije-Hückel Volume   The Debije-Hückel model calculates liquid molar volume for aqueous electrolyte solutions.

The equation for the Debije-Hückel volume model is:

$$V_m = x_w V_w^* + \sum_k x_k V_k$$

Where:

V_k^∞ is the molar volume for water and is calculated from the ASME steam table.

V_k is calculated from the Debije-Hückel limiting law for ionic species. It is assumed to be the infinite dilution partial volume for molecular solutes.

$$V_k = V_k^\infty + |z_k| 10^{-3} \left(\frac{A_V}{3b} \right) \ln\left(1 + bI^{\frac{1}{2}}\right)$$

Where:

V_k^∞	=	Partial molar ionic volume at infinite dilution
z_k	=	Charge number of ion k
A_V	=	Debije-Hückel constant for volume
b	=	1.2
I	=	$\frac{1}{2} \sum_k m_k z_k^2$ the ionic strength, with
m_k	=	Molarity of ion k

A_V is computed as follows:

$$A_V = -2 \times 10^6 A_\varphi R \left(3 \frac{\partial l \ln \varepsilon_w}{\partial p} + \frac{1}{p_w} \frac{\partial \rho_w}{\partial p} \right)$$

Where:

A_φ	=	Debije-Hückel constant for the osmotic coefficients (Pitzer, 1979) $$\frac{1}{3}\left(2\pi\left(10^{-3}\rho_w\right)N_A\right)^{\frac{1}{2}}\left(\frac{Q_e^2}{\varepsilon_w k_B T}\right)^{\frac{3}{2}}$$
ρ_w	=	Density of water $(\text{kg} / \text{m}^{-3})$
ε_w	=	Dielectric constant of water (Fm^{-1}, a function of pressure and temperature (Bradley and Pitzer, 1979)

Parameter Name	Applicable Components	Symbol	Default	Units
VLBROC	Ions, molecular Solutes	V_k^∞	0	MOLE-VOLUME

References

D. J. Bradley, K. S. Pitzer, "Thermodynamics of Electrolytes," *J. Phys. Chem.*, 83 (12), 1599 (1979).

H.C. Helgeson and D.H. Kirkham, "Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressure and temperature. I. Thermodynamic/electrostatic properties of the solvent", *Am. J. Sci.*, 274, 1089 (1974).

K.S. Pitzer, "Theory: Ion Interaction Approach," *Activity Coefficients in Electrolyte Solutions,* Pytkowicz, R. ed., Vol. I, (CRC Press Inc., Boca Raton, Florida, 1979).

Rackett/DIPPR/IK-CAPE Pure Component Liquid Volume

Three equations are available for pure component liquid molar volume: the Rackett equation, the DIPPR equation, and the IK-CAPE equation. The DIPPR equation is used if the parameter DNLDIP is available for a given component. The Rackett equation is used if the parameter RKTZRA is available. The IK-CAPE equation is used if the parameter VLPO is available.

For liquid molar volume of mixtures, the Rackett mixture equation is always used. This is not necessarily consistent with the pure component molar volume or density.

DIPPR

The DIPPR equation is:

$$\rho_i^{*,l} = C_{1i} / C_{2i}^{\left(1+(1-T/C_{3i})^{C_{4i}}\right)} \text{ for } C_{6i} \leq T \leq C_{7i}$$

$$V_i^{*,l} = \frac{1}{\rho_i^{*,l}}$$

This equation is similar to the Rackett equation. The model returns liquid molar volume for pure components.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
DNLDIP/1	C_{1i}	—	x	—	—	MOLE-DENSITY
DNLDIP/2	C_{2i}	0	x	—	—	—
DNLDIP/3	C_{3i}	T_{ci}	x	—	—	TEMPERATURE
DNLDIP/4	C_{4i}	0	x	—	—	—
DNLDIP/5	C_{5i}	0	x	—	—	—
DNLDIP/6	C_{6i}	0	x	—	—	TEMPERATURE
DNLDIP/7	C_{7i}	1000	x	—	—	TEMPERATURE

If element 3 is non-zero, absolute temperature units are assumed for element 3. (See Chapter 5.)

The IK-CAPE equation is:

$$V_i^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

for $C_{11i} \leq T \leq C_{12i}$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
VLPO/1	C_{1i}	—	X	—	—	MOLE-VOLUME
VLPO/2,…,10	C_{10i}	0	X	—	—	MOLE-VOLUME TEMPERATURE
VLPO/11	C_{11i}	0	X	—	—	TEMPERATURE
VLPO/12	C_{12i}	1000	X	—	—	TEMPERATURE

Rackett

The equation for the Rackett model is:

$$V_i^{*,l} = \frac{RT_{ci}\left(Z_i^{*,RA}\left[1+(1-T_r)^{2/7}\right]\right)}{p_{ci}}$$

Where:

$$T_r \quad = \quad \frac{T}{T_{ci}}$$

Parameter Name/ Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
PC	p_{ci}	—	—	10^5	10^8	PRESSURE
RKTZRA	$Z_i^{*,RA}$	ZC	x	0.1	1.0	—

References

H.G. Rackett, J.Chem, Eng. Data., Vol. 15, (1970), p. 514.

C.F. Spencer and R.P. Danner, J. Chem. Eng. Data, Vol. 17, (1972), p. 236.

Rackett/Campbell-Thodos Mixture Liquid Volume

The Rackett equation calculates liquid molar volume for all activity coefficient-based and petroleum-tuned equation-of-state based property methods. In the last category of property methods, the equation is used in conjunction with the API model. The API model is used for pseudocomponents, while the Rackett model is used for real components. (See API Liquid Volume .) Campbell-

Thodos is a variation on the Rackett model which allows the compressibility term $Z_i^{*,RA}$ to vary with temperature.

Rackett

The equation for the Rackett model is:

$$V_m^l = \frac{RT_c \left(Z_m^{RA} \right)^{\left[1 + \left(1 - T_r \right)^{2/7} \right]}}{P_c}$$

Where:

$$T_c \quad = \quad \sum_i \sum_j x_i x_j V_{ci} V_{cj} \left(T_{ci} T_{cj} \right)^{1/2} \left(1 - k_{ij} \right) \Big/ V_{cm}^2$$

$$\frac{T_c}{P_c} \quad = \quad \sum_i x_i \frac{T_{ci}}{P_{ci}}$$

$$Z_m^{RA} \quad = \quad \sum_i x_i Z_i^{*,RA}$$

$$V_{cm} \quad = \quad \sum_i x_i V_{ci}$$

$$T_r \quad = \quad \frac{T}{T_c}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
PC	p_{ci}	—	—	10^5	10^8	PRESSURE
VCRKT	V_{ci}	VC	x	0.001	3.5	MOLE-VOLUME
RKTZRA	$Z_i^{*,RA}$	ZC	x	0.1	1.0	—
RKTKIJ	k_{ij}	$1 - \dfrac{8 \left(V_{ci} V_{cj} \right)^{1/2}}{\left(V_{ci}^{1/3} + V_{cj}^{1/3} \right)^3}$	x	-5.0	5.0	—

Campbell-Thodos

The Campbell-Thodos model uses the same equation and parameters as the Rackett model, above, except that Z_m^{RA} is allowed to vary with temperature:

$$Z_m^{RA} \quad = \quad \sum_i x_i Z_i^{*,RA} [1 + d_i (1 - T_r)]$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
RACKET/3	di	none	x	0	0.11	—

The Campbell-Thodos model is used when RACKET/3 is set to a value less than 0.11. The default value, 2/7, indicates that the standard Rackett equation should used. When Campbell-Thodos is not used, RACKET/3 should be kept at its default value of 2/7 for all components.

References

H.G. Rackett, *J.Chem, Eng. Data.*, Vol. 15, (1970), p. 514.

C.F. Spencer and R.P. Danner, *J. Chem. Eng. Data*, Vol. 17, (1972), p. 236.

Modified Rackett

The Modified Rackett equation improves the accuracy of liquid mixture molar volume calculation by introducing additional parameters to compute the pure component parameter RKTZRA and the binary parameter k_{ij}.

The equation for the Modified Rackett model is:

$$V_m^l = \frac{RT_c \left(Z_m^{RA} \right)^{\left[1 + \left(1 - T_r \right)^{2/7} \right]}}{P_c}$$

Where:

$$T_c \quad = \quad \sum_i \sum_j x_i x_j V_{ci} V_{cj} \left(T_{ci} T_{cj} \right)^{1/2} \left(1 - k_{ij} \right) \Big/ V_{cm}^2$$

$$k_{ij} \quad = \quad A_{ij} + B_{ij} T + C_{ij} T^2$$

$$\frac{T_c}{P_c} \quad = \quad \sum_i x_i \frac{T_{ci}}{P_{ci}}$$

$$Z_m^{RA} \quad = \quad \sum_i x_i Z_i^{*,RA}$$

$$Z_i^{*,RA} \quad = \quad a_i + b_i T + c_i T^2$$

$$V_{cm} \quad = \quad \sum_i x_i V_{ci}$$

$$T_r \quad = \quad \frac{T}{T_c}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MRKZRA/1	a_i	RKTZRA	x	0.1	0.5	—
MRKZRA/2	b_i	0	x	—	—	—
MRKZRA/3	c_i	0	x	—	—	—
MRKKIJ/1	A_{ij}	$1 - \dfrac{8\left(V_{ci}V_{cj}\right)^{1/2}}{\left(V_{ci}^{1/3} + V_{cj}^{1/3}\right)^3}$	x	—	—	—
MRKKIJ/2	B_{ij}	0	x	—	—	—
MRKKIJ/3	C_{ij}	0	x	—	—	—

References

H.G. Rackett, *J.Chem, Eng. Data.*, Vol. 15, (1970), p. 514.

C.F. Spencer and R.P. Danner, *J. Chem. Eng. Data*, Vol. 17, (1972), p. 236.

Aspen/IK-CAPE Solids Volume

Two equations are available for pure component solid molar volume.

The Aspen Physical Property System uses this equation	When this parameter is available for a given component
Aspen	VSPOLY
IK-CAPE	VSPO

Aspen Polynomial

The equation for the Aspen solids volume polynomial is:

$$V_i^{*,s} = C_{1i} + C_2 T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 \text{ for } C_{6i} \leq T \leq C_{7i}$$

Parameter Name	Applicable Components	Symbol	MDS	Default	Units
VSPOLY/1	Salts, CI solids	C_{1i}	x	—	MOLE-VOLUME TEMPERATURE
VSPOLY/2, . . . , 5	Salts, CI solids	$C_{2i},...,C_{5i}$	x	0	MOLE-VOLUME TEMPERATURE
VSPOLY/6	Salts, CI solids	C_{6i}	x	0	MOLE-VOLUME TEMPERATURE
VSPOLY/7	Salts, CI solids	C_{7i}	x	1000	MOLE-VOLUME TEMPERATURE

IK-CAPE Equation

The IK-CAPE equation is a polynomial equation containing 10 terms. If the parameter VSPO is available, the Aspen Physical Property System uses the IK-CAPE equation.

$$V_i^{*,s} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

for $C_{11i} \leq T \leq C_{12i}$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
VSPO/1	C_{1i}	—	X	—	—	MOLE-VOLUME
VSPO/2,…,10	C_{10i}	0	X	—	—	MOLE-VOLUME TEMPERATURE
VSPO/11	C_{11i}	0	X	—	—	TEMPERATURE
VSPO/12	C_{12i}	1000	X	—	—	TEMPERATURE

Heat Capacity Models

The Aspen Physical Property System has five built-in heat capacity models. This section describes the heat capacity models available.

Model	Type
Aqueous Infinite Dilution Heat Capacity Polynomial	Electrolyte liquid
Criss-Cobble Aqueous Infinite Dilution Ionic Heat Capacity	Electrolyte liquid
DIPPR/IK-CAPE Liquid Heat Capacity	Liquid
Ideal Gas Heat Capacity/DIPPR	Ideal gas
Solids Heat Capacity Polynomial	Solid
IK-CAPE Heat Capacity Polynomial	Ideal gas, Liquid and Solid

Aqueous Infinite Dilution Heat Capacity

The aqueous phase infinite dilution enthalpies, entropies, and Gibbs energies are calculated from the heat capacity polynomial. The values are used in the calculation of aqueous and mixed solvent properties of electrolyte solutions:

$$C_{p,i}^{\infty,aq} = C_1 + C_2T + C_{3i}T^2 + \frac{C_{4i}}{T} + \frac{C_{5i}}{T^2} + \frac{C_{6i}}{\sqrt{T}} \text{ for } C_{7i} \leq T \leq C_{8i}$$

$C_{p,i}^{\infty,aq}$ is linearly extrapolated using the slope at C_{7i} for $T < C_{7i}$

$C_{p,i}^{\infty,aq}$ is linearly extrapolated using the slope at C_{8i} for $T > C_{8i}$

Parameter Name/Element	Applicable Components	Symbol	Default
CPAQ0	Ions, molecular solutes	C_{1i}	—
CPAQ0	Ions, molecular solutes	$C_{2i},\ldots,C_{5i}$	0
CPAQ0	Ions, molecular solutes	C_{6i}	0
CPAQ0	Ions, molecular solutes	C_{7i}	1000

The units are TEMPERATURE and HEAT CAPACITY.

Criss-Cobble Aqueous Infinite Dilution Ionic Heat Capacity

The Criss-Cobble correlation for aqueous infinite dilution ionic heat capacity is used if no parameters are available for the aqueous infinite dilution heat capacity polynomial. From the calculated heat capacity, the thermodynamic properties entropy, enthalpy and Gibbs energy at infinte dilution in water are derived:

$$C_{p,i}^{\infty,aq} = f\left(\left(S_a^{\infty,aq}(T = 298) \text{ or } S_c^{\infty,aq}(T = 298), ion\ type, T\right)\right)$$

Parameter Name	Applicable Components	Symbol	Default	Units
IONTYP	Ions	Ion Type	0	—
SO25C	Anions	$S_a^{\infty,aq}$	$\dfrac{\Delta_f H_a^{\infty,aq}(T - 298) - \Delta_f G_a^{\infty,aq}(T = 298)}{298.15}$	MOLE-ENTROPY
	Cations	$S_a^{\infty,aq}$	$\dfrac{\Delta_f H_a^{\infty,aq}(T - 298) - \Delta_f G_a^{\infty,aq}(T = 298)}{298.15}$	MOLE-ENTROPY

DIPPR/IK-CAPE Liquid Heat Capacity

The DIPPR/IK-CAPE liquid heat capacity model is used to calculate pure component liquid heat capacity and pure component liquid enthalpy. To use this model, two conditions must exist:

- The parameter CPLDIP or CPLIKC is available.

- The component is not supercritical (HENRY-COMP).

The model uses a specific method (see Chapter 4):

$$H_i^{*,l}(T) - H_i^{*,l}(T^{ref}) = \int_{T^{ref}}^{T} C_{p,i}^{*,l} dT$$

$H_i^{*,l}(T^{ref})$ is calculated as:

$$H_i^{*,l}(T^{ref}) = H_i^{*,ig} + \left(H_i^{*,v} - H_i^{*,ig}\right) - \Delta_{vap} H_i^{*,l}$$

T^{ref} is the reference temperature; it defaults to 298.15 K. You can enter a different value for the reference temperature. This is useful when you want to use this model for very light components or for components that are solids at 298.15K.

Activate this method by specifying the route DHL09 for the property DHL on the Properties Property Methods Routes sheet. For equation-of-state property method, you must also modify the route for the property DHLMX to use a route with method 2 or 3, instead of method 1. For example, you can use the route DHLMX00 or DHLMX30. You must ascertain that the route for DHLMX that you select contains the appropriate vapor phase model and heat of mixing calculations. Click the View button on the form to see details of the route.

Optionally, you can specify that this model is used for only certain components. The properties for the remaining components are then calculated by the standard model. Use the parameter COMPHL to specify the components for which this model is used. By default, all components with the CPLDIP or CPLIKC parameters use this model.

If this parameter is available	The Aspen Physical Property System uses this equation
CPLDIP	DIPPR
CPLIKL	IK-CAPE

DIPPR Liquid Heat Capacity

The DIPPR equation is:

$$C_{p,i}^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 \ \ for \ C_{6i} \le T \le C_{7i}$$

Linear extrapolation occurs for $C_p^{*,l}$ versus T outside of bounds.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
CPLDIP/1	C_{1i}	— T	x	—	—	MOLE-HEAT-CAPACITY, TEMPERATURE
CPLDIP/2,...,5	$C_{2i},\ldots,C_{5i}$	0	x	—	—	MOLE-HEAT-CAPACITY, TEMPERATURE
CPLDIP/6	C_{6i}	0	x	—	—	TEMPERATURE
CPLDIP/7	C_{7i}	1000	x	—	—	TEMPERATURE
TREFHL	T^{ref}	298.15	—	—	—	TEMPERATURE
COMPHL	—	—	—	—	—	—

To specify that the model is used for a component, enter a value of 1.0 for COMPHL.

IK-CAPE Liquid Heat Capacity

The IK-CAPE equation is:

$$C_{p,i}^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + \frac{C_{5i}}{T^2} \ for \ C_{6i} \le T \le C_{7i}$$

Linear extrapolation occurs for $C_p^{*,l}$ versus T outside of bounds.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
CPLIKC/1	C_{1i}	— T	x	—	—	MOLE-HEAT-CAPACITY
CPLIKC/2,...,4	$C_{2i},...,C_{4i}$	0	x	—	—	MOLE-HEAT-CAPACITY, TEMPERATURE
CPLIKC/5	C_{5i}	0	x	—	—	MOLE-HEAT-CAPACITY, TEMPERATURE
CPLIKC/6	C_{6i}	0	x	—	—	TEMPERATURE
CPLIKC/7	C_{7i}	1000	x	—	—	TEMPERATURE

If element 5 is non-zero, absolute temperature units are assumed.

Ideal Gas Heat Capacity/DIPPR

The DIPPR ideal gas heat capacity equation is used for most components in the Aspen Physical Property System pure components databank. It is used when the parameter CPIGDP is available for a given component.

DIPPR

The equation for the DIPPR ideal gas heat capacity model by Aly and Lee 1981 is:

$$C_p^{*,ig} = C_{1i} + C_{2i}\left(\frac{C_{3i}/T}{\sinh(C_{3i}/T)}\right)^2 + C_{4i}\left(\frac{C_{5i}/T}{\cosh(C_{5i}/T)}\right)^2 \text{ for } C_{6i} \leq T \leq C_{7i}$$

This model is also used to calculate ideal gas enthalpies, entropies, and Gibbs energies.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
CPIGDP/1	C_{1i}	—	x	—	—	MOLE-HEAT-CAPACITY
CPIGDP/2	C_{2i}	0	x	—	—	MOLE-HEAT-CAPACITY
CPIGDP/3	C_{3i}	0	x	—	—	TEMPERATURE
CPIGDP/4	C_{4i}	0	x	—	—	MOLE-HEAT-CAPACITY
CPIGDP/5	C_{5i}	0	x	—	—	TEMPERATURE
CPIGDP/6	C_{6i}	0	x	—	—	TEMPERATURE
CPIGDP/7	C_{7i}	1000	x	—	—	TEMPERATURE

If elements 3 or 5 of CPIGDP are non-zero, absolute temperature units are assumed.

Ideal Gas Heat Capacity Polynomial

The ideal gas heat capacity polynomial is used for components stored in ASPENPCD, AQUEOUS, and SOLIDS databanks. This model is also used in PCES.

$$C_p^{*,ig} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 \text{ for } C_{7i} \leq T \leq C_{8i}$$

$$C_p^{*,ig} = C_{9i} + C_{10i}T^{C_{11i}} \text{ for } T < C_{7i}$$

$C_p^{*,ig}$ is linearly extrapolated using slope at C_{8i} for $T > C_{8i}$

This model is also used to calculate ideal gas enthalpies, entropies, and Gibbs energies.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
CPIG/1	C_{1i}	—	—	—	—	MOLE-HEAT-CAPACITY, TEMPERATURE
CPIG/2, . . . , 6	$C_{2i}, ..., C_{6i}$	0	—	—	—	MOLE-HEAT-CAPACITY, TEMPERATURE
CPIG/7	C_{7i}	0	—	—	—	TEMPERATURE
CPIG/8	C_{8i}	1000	—	—	—	TEMPERATURE
CPIG/9, 10, 11	C_{9i}, C_{10i}, C_{11i}	—	—	—	—	MOLE-HEAT-CAPACITY, TEMPERATURE

If elements 10 or 11 of CPIG are non-zero, absolute temperature units are assumed for elements 9 through 11.

References

Data for the Ideal Gas Heat Capacity Polynomial: Reid, Prausnitz and Poling, The Properties of Gases and Liquids, 4th ed., (New York: McGraw-Hill, 1987).

The Aspen Physical Property System combustion data bank, JANAF Thermochemical Data, Compiled and calculated by the Thermal Research Laboratory of Dow Chemical Company.

F. A. Aly and L. L. Lee, "Self-Consistent Equations for Calculating the Ideal Gas Heat Capacity, Enthalpy, and Entropy, Fluid Phase Eq., Vol. 6, (1981), p. 169.

Solids Heat Capacity Polynomial

The enthalpy, entropy, and Gibbs energy of solids are calculated from the heat capacity polynomial:

$$C_{p,i}^{*,s} = C_{1i} + C_{2i}T + C_{3i}T^2 + \frac{C_{4i}}{T} + \frac{C_{5i}}{T^2} + \frac{C_{6i}}{\sqrt{T}} \text{ for } C_{7i} \leq T \leq C_{8i}$$

$C_{p,i}^{*,8}$ linearly extrapolated using the slope at C_{7i} for $T < C_{7i}$ and

$C_{p,i}^{*,8}$ linearly extrapolated using the slope at C_{8i} for $T > C_{8i}$

Parameter Name	Applicable Components	Symbol	MDS	Default
CPSPO1/1	Solids, Salts	C_{1i}	x	—
CPSPO1/2, . . . , 6	Solids, Salts	$C_{2i}, ..., C_{6i}$	x	0
CPSPO1/7	Solids, Salts	C_{7i}	x	0
CPSPO1/8	Solids, Salts	C_{8i}	x	1000

If elements 4, 5, or 6 are non-zero, absolute temperature units are assumed for elements 1 through 6.

The units are TEMPERATURE and HEAT CAPACITY.

IK-CAPE Heat Capacity Polynomial

If the parameters CPIGPO or CPLPO or CPSPO are available, the IK-CAPE heat capacity polynomial is used to calculate either:

- Pure component ideal gas heat capacity and enthalpy (CPIGPO)
- Liquid heat capacity and enthalpy (CPLPO)
- Solid heat capacity and enthalpy (CPSPO)

The equation is:

$$C_p^* = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

for $C_{11i} \leq T \leq C_{12i}$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
CPIGPO/1 CPLPO/1 CPSPO/1	C_{1i}	—	X	—	—	MOLE-CAPACITY
CPIGPO/2,…,10 CPLPO/2,…,10 CPSPO/2,…,10	C_{10i}	0	X	—	—	MOLE-CAPACITY TEMPERATURE
CPIGPO/11 CPLPO/11 CPSPO/11	C_{11i}	0	X	—	—	TEMPERATURE
CPIGPO/12 CPLPO/12 CPSPO/12	C_{12i}	1000	X	—	—	TEMPERATURE

Solubility Correlations

The Aspen Physical Property System has two built-in solubility correlation models. This section describes the solubility correlation models available.

Model	Type
Henry's constant	Gas solubility in liquid
Water solubility	Water solubility in organic liquid

Henry's Constant

The Henry's constant model is used when Henry's Law is applied to calculate K-values for dissolved gas components in a mixture. Henry's Law is available in all activity coefficient property methods, such as the WILSON property method. The model calculates Henry's constant for a dissolved gas component (i) in one or more solvents (A or B):

$$\ln\left(H_i/\gamma_i^\infty\right) = \sum_A w_A \ln\left(H_{iA}/\gamma_{iA}^\infty\right)$$

Where:

$$w_A = \frac{x_A\left(V_{cA}\right)^{2/3}}{\sum_B x_B\left(V_{cB}\right)^{2/3}}$$

$$\ln H_{iA}\left(T, p_A^{*,l}\right) = a_{iA} + b_{iA}/T + c_{iA} \ln T + d_{iA}T \text{ for } T_L \leq T \leq T_H$$

$$H_{iA}(T, P) = H_{iA}\left(T, p_A^{*,l}\right) \exp\left(\frac{1}{RT} \int_{p_a^{*,l}}^{p} V_{iA}^\infty \, dp\right)$$

The parameter V_{iA}^∞ is obtained from the Brelvi-O'Connell model. $p_A^{*,l}$ is obtained from the Antoine model. γ^∞ is obtained from the appropriate activity coefficient model.

The Henry's constants a_{iA}, b_{iA}, c_{iA}, and d_{iA} are specific to a solute-solvent pair. They can be obtained from regression of gas solubility data. The Aspen Physical Property System has a large number of built-in Henry's constants for many solutes in solvents. These parameters were obtained using data from the Dortmund Databank. See Physical Property Data, Chapter 1, for details.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
VC	V_{cA}	—	—	0.001	3.5	MOLE-VOLUME
HENRY/1	a_{iA}	—	x	—	—	PRESSURE, TEMPERATURE
HENRY/2	b_{iA}	0	x	—	—	TEMPERATURE
HENRY/3	c_{iA}	0	x	—	—	TEMPERATURE
HENRY/4	d_{iA}	0	x	—	—	TEMPERATURE
HENRY/5	T_L	0	x	—	—	TEMPERATURE
HENRY/6	T_H	2000	x	—	—	TEMPERATURE

If a_{iA} is missing, $\ln\dfrac{H_{iA}}{\gamma_{iA}^\infty}$ is set to zero and the weighting factor w_A is renormalized.

If elements 2 or 3 are non-zero, absolute temperature units are assumed for elements 1 through 4.

Water Solubility

This model calculates solubility of water in a hydrocarbon-rich liquid phase. The model is used automatically when you model a hydrocarbon-water system with the free-water option. See Chapter 6 for details.

The expression for the liquid mole fraction of water in the ith hydrocarbon species is:

$$\ln x_{wi} = C_{1i} + \frac{C_{2i}}{T} + C_{3i}T \text{ for } C_{4i} \leq T \leq C_{5i}$$

The parameters for 60 hydrocarbon components are stored in the Aspen Physical Property System pure component databank.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
WATSOL/1	C_{1i}	$fcn(T_{bi}, ASG_i, M_i)$	—	-10.0	33.0	TEMPERATURE
WATSOL/2	C_{2i}	$fcn(T_{bi}, ASG_i, M_i)$	—	-10000.0	3000.0	TEMPERATURE
WATSOL/3	C_{3i}	0	—	-0.05	0.05	TEMPERATURE
WATSOL/4	C_{4i}	0	—	0.0	500	TEMPERATURE
WATSOL/5	C_{5i}	1000	—	4.0	1000	TEMPERATURE

Absolute temperature units are assumed for elements 1 through 4.

Other Thermodynamic Property Models

The Aspen Physical Property System has four built-in additional thermodynamic property models that do not fit in any other category. This section describes these models:

- Cavett Liquid Enthalpy Departure
- BARIN Equations for Gibbs Energy, Enthalpy, Entropy and Heat Capacity
- Electrolyte NRTL Enthalpy
- Electrolyte NRTL Gibbs Energy
- Liquid Enthalpy from Liquid Heat Capacity Correlation
- Enthalpies Based on Different Reference States
- Helgeson Equations of State

Cavett

The general form for the Cavett model is:

$$\left(H_i^{*,l} - H_i^{*,ig}\right) = fcn\left(T, T_{ci}, p, p_{ci}, Z_{\lambda i}^*\right)$$

$$\left(H_m^l - H_m^{ig}\right) = \sum_i x_i \left(H_i^{*,l} - H_i^{*,ig}\right)$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
PC	p_{ci}	—	—	10^5	10^8	PRESSURE
DHLCVT	$Z_{\lambda,i}^\infty$	ZC	X	0.1	0.5	—

BARIN Equations for Gibbs Energy, Enthalpy, Entropy, and Heat Capacity

The following equations are used when parameters from the Aspen Physical Property System inorganic databank are retrieved.

- Gibbs energy:

$$G_i^{*,\alpha} = a_{n,i}^\alpha + b_{n,i}^\alpha T + c_{n,i}^\alpha (T \ln T) + d_{n,i}^\alpha T^2 + e_{n,i}^\alpha T^3 + f_{n,i}^\alpha T^4 + g_{n,i}^\alpha T^{-1} + h_{n,i}^\alpha T^{-2} \quad (1)$$

- Enthalpy:

$$H_i^{*,\alpha} = a_{n,i}^\alpha - c_{n,i}^\alpha T - d_{n,i}^\alpha T^2 - 2e_{n,i}^\alpha T^3 - 3f_{n,i}^\alpha T^4 + 2g_{n,i}^\alpha T^{-1} + 3h_{n,i}^\alpha T^{-2} \quad (2)$$

- Entropy:

$$S_i^{*,\alpha} = -b_{n,i}^\alpha - c_{n,i}^\alpha (1 + \ln T) - 2d_{n,i}^\alpha T - 3e_{n,i}^\alpha T^2 - 4f_{n,i}^\alpha T^3 + g_{n,i}^\alpha T^{-2} + 2h_{n,i}^\alpha T^{-3} \quad (3)$$

- Heat capacity:

$$C_{p,i}^{*,\alpha} = -c_{n,i}^\alpha - 2d_{n,i}^\alpha T - 6e_{n,i}^\alpha T^2 - 12f_{n,i}^\alpha T^3 - 2g_{n,i}^\alpha T^{-2} - 6h_{n,i}^\alpha T^{-3} \quad (4)$$

α refers to an arbitrary phase which can be solid, liquid, or ideal gas. For each phase, multiple sets of parameters from 1 to n are present to cover multiple temperature ranges. The value of the parameter n depends on the phase. (See tables that follow.)

The four properties C_p, H, S, and G are interrelated as a result of the thermodynamic relationships:

$$H_i^{*,\alpha}(T) - H_i^{*,\alpha}\left(T^{ref}\right) = \int_{T^{ref}}^{T} C_{p,i}^{*,\alpha} dT$$

$$S_i^{*,\alpha}(T) - S_i^{*,\alpha}\left(T^{ref}\right) = \int_{T^{ref}}^{T} \frac{C_{p,i}^{*,\alpha}}{T} dT$$

$$G_i^{*,\alpha} = H_i^{*,\alpha} - TS_i^{*,\alpha}$$

There are analytical relationships between the expressions describing the properties C_p, H, S, and G (equations 1 to 4). The parameters $a_{n,i}$ to $h_{n,i}$ can occur in more than one equation.

Solid Phase

The parameters in range n are valid for temperature:
$$T_{n,l}^s < T < T_{n,h}^s$$

Parameter Name /Element †	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
CPSXPn/1	$T_{n,l}^s$	—	x	—	—	TEMPERATURE
CPSXPn/2	$T_{n,h}^s$	—	x	—	—	TEMPERATURE
CPSXPn/3	$a_{n,i}^s$	—	x	—	—	††
CPSXPn/4	$b_{n,i}^s$	0	x	—	—	††
CPSXPn/5	$c_{n,i}^s$	0	x	—	—	††
CPSXPn/6	$d_{n,i}^s$	0	x	—	—	††
CPSXPn/7	$e_{n,i}^s$	0	x	—	—	††
CPSXPn/8	$f_{n,i}^s$	0	x	—	—	††
CPSXPn/9	$g_{n,i}^s$	0	x	—	—	††
CPSXPn/10	$h_{n,i}^s$	0	x	—	—	††

† n is 1 through 7. CPSXP1 vector stores solid parameters for the first temperature range. CPSXP2 vector stores solid parameters for the second temperature range, and so on.

†† TEMPERATURE, ENTHALPY, ENTROPY

Liquid Phase

The parameters in range *n* are valid for temperature: $T_{n,l}^l < T < T_{n,h}^l$

Parameter Name /Element †	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
CPLXPn/1	$T_{n,l}^l$	—	x	—	—	TEMPERATURE
CPLXPn/2	$T_{n,h}^l$	—	x	—	—	TEMPERATURE
CPLXPn/3	$a_{n,i}^l$	—	x	—	—	††
CPLXPn/4	$b_{n,i}^l$	0	x	—	—	††
CPLXPn/5	$c_{n,i}^l$	0	x	—	—	††
CPLXPn/6	$d_{n,i}^l$	0	x	—	—	††
CPLXPn/7	$e_{n,i}^l$	0	x	—	—	††
CPLXPn/8	$f_{n,i}^l$	0	x	—	—	††
CPLXPn/9	$g_{n,i}^l$	0	x	—	—	††
CPLXPn/10	$h_{n,i}^l$	0	x	—	—	††

† n is 1 through 2. CPLXP1 stores liquid parameters for the first temperature range. CPLXP2 stores liquid parameters for the second temperature range.

†† TEMPERATURE, ENTHALPY, ENTROPY

Ideal Gas Phase

The parameters in range n are valid for temperature: $T_{n,l}^{ig} < T < T_{n,h}^{ig}$

Parameter Name /Element †	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
CPIXPn/1	$T_{n,l}^{ig}$	—	x	—	—	TEMPERATURE
CPIXPn/2	$T_{n,l}^{ig}$	—	x	—	—	TEMPERATURE
CPIXPn/3	$a_{n,i}^{ig}$	—	x	—	—	††
CPIXPn/4	$b_{n,i}^{ig}$	0	x	—	—	††
CPIXPn/5	$c_{n,i}^{ig}$	0	x	—	—	††
CPIXPn/6	$d_{n,i}^{ig}$	0	x	—	—	††
CPIXPn/7	$e_{n,i}^{ig}$	0	x	—	—	††
CPIXPn/8	$f_{n,i}^{ig}$	0	x	—	—	††
CPIXPn/9	$g_{n,i}^{ig}$	0	x	—	—	††
CPIXPn/10	$h_{n,i}^{ig}$	0	x	—	—	††

† n is 1 through 3. CPIXP1 vector stores ideal gas parameters for the first temperature range. CPIXP2 vector stores ideal gas parameters for the second temperature range, and so on.

†† TEMPERATURE, ENTHALPY, ENTROPY

Electrolyte NRTL Enthalpy

The equation for the electrolyte NRTL enthalpy model is:

$$H_m^* = x_w H_w^* + \sum_k x_k H_k^\infty + H_m^{*E}$$

The molar enthalpy H_m^* and the molar excess enthalpy H_m^{*E} are defined with the asymmetrical reference state: the pure solvent water and infinite dilution of molecular solutes and ions. (here * refers to the asymmetrical reference state.)

H_w^* is the pure water molar enthalpy, calculated from the Ideal Gas model and the ASME Steam Table equation-of-state. (here * refers to pure component.)

$$H_w^* = \Delta H_f^{*,ig}(T = 298.15) + \int_{298.15}^{T} C_{p,k}^{ig} dT + \left(H_w(T,p) - H_w^{ig}(T,p) \right)$$

The property H_k^∞ is calculated from the infinite dilution aqueous phase heat capacity polynomial model, by default. If polynomial

model parameters are not available, it is calculated from the Criss-Cobble model for ions and from Henry's law for molecular solutes.

The subscript k can refer to a molecular solute *(i)*, to a cation *(c)*, or an anion *(a)*:

$$H_k^\infty = \Delta_f H_k^{\infty,aq} + \int_{298.15}^{T} C_{p,k}^{\infty,aq}$$

H_m^{*E} is excess enthalpy and is calculated from the electrolyte NRTL activity coefficient model.

See Criss-Cobble model and Henry's law model, this chapter, for more information.

Parameter Name	Applicable Components	Symbol	Default	Units
IONTYP	Ions	Ion	0	—
SO25C	Cations	$S_c^{\infty,aq}(T=298)$	—	MOLE-ENTROPY
	Anions	$S_a^{\infty,aq}(T=298)$	—	MOLE-ENTROPY
DHAQFM	Ions, Molecular Solutes	$\Delta_f H_k^{\infty,aq}$	—	MOLE-ENTHALPY
CPAQ0	Ions, Molecular Solutes	$C_{p,k}^{\infty,aq}$	—	HEAT-CAPACITY
DHFORM	Molecular Solutes	$\Delta_f H_i^{*,ig}$	—	MOLE-ENTHALPY
	Water	$\Delta_f H_w^{*,ig}$	—	MOLE-ENTHALPY
CPIG	Molecular Solutes	$C_{p,i}^{*,ig}$	—	See note
	Water	$C_{p,w}^{*,ig}$	—	See note

IONTYP is not needed if CPAQ0 is given for ions.

DHFORM is not needed if DHAQFM and CPAQ0 are given for molecular solutes.

The unit keywords for CPIG are TEMPERATURE and HEAT-CAPACITY. If elements 10 or 11 of CPIG are non-zero, absolute temperature units are assumed for all elements.

Electrolyte NRTL Gibbs Energy

The equation for the NRTL Gibbs energy model is:

$$G_m^* = x_w \mu_w^* + \sum_k x_k \mu_k^\infty + \sum_j x_j \ln x_j + G_m^{*E}$$

The molar Gibbs energy and the molar excess Gibbs energy G_m^* and G_m^{*E} are defined with the asymmetrical reference state: as pure water and infinite dilution of molecular solutes and ions. (* refers to the asymmetrical reference state.) The ideal mixing term is calculated normally, where *j* refers to any component. The molar

Gibbs energy of pure water (or thermodynamic potential) μ_w^* is calculated from the ideal gas contribution. This is a function of the ideal gas heat capacity and the departure function. (here * refers to the pure component.)

$$\mu_w^* = \mu_w^{*,ig} + \left(\mu_w^* - \mu_w^{*,ig}\right)$$

The departure function is obtained from the ASME steam tables.

The aqueous infinite dilution thermodynamic potential μ_k^∞ is calculated from the infinite dilution aqueous phase heat capacity polynomial model, by default. k refers to any ion or molecular solute. If polynomial model parameters are not available, it is calculated from the Criss-Cobble model for ions and from Henry's law for molecular solutes:

$$\mu_k^\infty = fcn\left(\Delta_f G_k^{\infty,aq}, C_{pk}^{\infty,aq}\right)$$

G^{*E} is calculated from the electrolyte NRTL activity coefficient model.

See the Criss-Cobble model and Henry's law model, this chapter, for more information.

Parameter Name	Applicable Components	Symbol	Default	Units
IONTYP	Ions	Ion	0	—
SO25C	Cations	$S_c^{\infty,aq}(T = 298)$	—	MOLE-ENTROPY
	Anions	$S_a^{\infty,aq}(T = 298)$	—	MOLE-ENTROPY
DGAQFM	Ions, molecular solutes	$\Delta_f G_k^{\infty,aq}$	—	MOLE-ENTHALPY
CPAQ0	Ions, molecular solutes	$C_{p,k}^{\infty,aq}$	—	HEAT-CAPACITY
DGFORM	Molecular solutes	$\Delta_f G_i$	—	MOLE-ENTHALPY
	Water	$\Delta_f G_w$	—	MOLE-ENTHALPY
CPIG	Molecular solutes	$C_{p,i}^{*,ig}$	—	See note.
	Water	$C_{p,w}^{*,ig}$	—	See note.

IONTYP and SO25C are not needed if CPAQ0 is given for ions.

DGFORM is not needed if DHAQFM and CPAQ0 are given for molecular solutes.

The unit keywords for CPIG are TEMPERATURE and HEAT-CAPACITY. If elements 10 or 11 of CPIG are non-zero, absolute temperature units are assumed for all elements.

Liquid Enthalpy from Liquid Heat Capacity Correlation

Liquid enthalpy is directly calculated by integration of liquid heat capacity:

$$H_i^{*,l}(T) = H_i^{*,l}(T^{ref}) + \int_{T^{ref}}^{T} C_{p,i}^{*,l} dT$$

The reference enthalpy is calculated at T^{ref} as:

$$H_i^{*,l}(T^{ref}) = H_i^{*,ig} + \left(H_i^{*,v} - H_i^{*,ig}\right) - \Delta_{vap} H_i^{*,l}$$

Where:

$H_i^{*,ig}$	=	Ideal gas enthalpy
$H_i^{*,v} - H_i^{*,ig}$	=	Vapor enthalpy departure from equation-of-state
$\Delta_{vap} H_i^{*,l}$	=	Heat of vaporization from Watson/DIPPR/IK-CAPE model
T^{ref}	=	Reference temperature, specified by user. Defaults to 298.15 K

See DIPPR/IK-CAPE Liquid Heat Capacity for parameter requirement and additional details.

Enthalpies Based on Different Reference States

Two property methods, WILS-LR and WILS-GLR, are available to calculate enthalpies based on different reference states. The WILS-LR property method is based on saturated liquid reference state for all components. The WILS-GLR property method allows both ideal gas and saturated liquid reference states.

These property methods use an enthalpy method that optimizes the accuracy tradeoff between liquid heat capacity, heat of vaporization, and vapor heat capacity at actual process conditions. This highly recommended method eliminates many of the problems associated with accurate thermal properties for both phases, especially the liquid phase.

The liquid enthalpy of mixture is calculated by the following equation (see the table labeled Liquid Enthalpy Methods):

$$H_m^l = H_m^{ig} + \left(H_m^l - H_m^{ig}\right)$$

Where:

H_m^{ig}	=	Enthalpy of ideal gas mixture
	=	$\sum_i x_i H_i^{*,ig}$
$H_i^{*,ig}$	=	Ideal gas enthalpy of pure component i
$\left(H_m^l - H_m^{ig}\right)$	=	Enthalpy departure of mixture

For supercritical components, declared as Henry's components, the enthalpy departure is calculated as follows:

$$H_m^l - H_m^{ig} = -RT^2 \sum_i x_i \left(\frac{\delta \ln \Phi_i^l}{\delta T} \right)$$

For subcritical components:

$$H_m^l - H_m^{ig} = \sum_A x_A \left(H_A^{*,l} - H_A^{*,ig} \right) + H_m^{E,l}$$

$$H_m^{E,l} = -RT^2 \sum_B x_B \left(\frac{\delta \ln \gamma_B}{\delta T} \right)$$

$$H_A^{*,l} - H_A^{*,ig} = \text{Enthalpy departure of pure component A}$$

$H^{*,ig}$ and $H^{*,l}$ can be calculated based on either saturated liquid or ideal gas as reference state.

Saturated Liquid as Reference State

The saturated liquid enthalpy at temperature T is calculated as follows:

$$H_i^{*,l} = H_i^{ref,l} + \int_{T_i^{ref,l}}^{T} C_{p,i}^{*,l} dT$$

Where:

$$H_i^{ref,l} = \text{Reference enthalpy for liquid state at } T_i^{ref,l}$$

$$= 0 \text{ at } T_i^{ref,l} \text{ of 273.15 K by default}$$

$$C_{p,i}^{*,l} = \text{Liquid heat capacity of component i}$$

The ideal gas enthalpy at temperature T is calculated from liquid enthalpy as follows:

$$H_i^{*,ig} = H_i^{ref,l} + \int_{T_i^{ref,l}}^{T_i^{con,l}} C_{p,i}^{*,l} dT + \Delta_{vap} H_i^* \left(T_i^{con,l} \right) - \Delta H_{v,i}^* \left(T_i^{con,l}, p_i^{*,l} \right) + \int_{T_i^{con,l}}^{T} C_{p,i}^{*,ig} dT$$

Where:

$T_i^{con,l}$	=	Temperature of conversion from liquid to vapor enthalpy for component i
$\Delta_{vap} H_i^* \left(T_i^{con,l} \right)$	=	Heat of vaporization of component i at temperature of $T^{con,l}$
$\Delta H_{v,i}^* \left(T^{con,l}, p_i^{*,l} \right)$	=	Vapor enthalpy departure of component i at the conversion temperature and vapor pressure $p_i^{*,l}$
$p_i^{*,l}$	=	Liquid vapor pressure of component i

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

$T_i^{con,l}$ is the temperature at which one crosses from liquid state to the vapor state. This is a user-defined temperature that defaults to the system temperature T. $T_i^{con,l}$ may be selected such that heat of vaporization for component i at the temperature is most accurate.

The vapor enthalpy is calculated from ideal gas enthalpy as follows:

$$H_i^{*,v} = H_i^{*,ig} + \Delta H_{v,i}^*(T,P)$$

Where:

$$\Delta H_{v,i}^*(T,P)$$ = Vapor enthalpy departure of pure component i at the system temperature and pressure

The liquid heat capacity and the ideal gas heat capacity can be calculated from the ASPEN, DIPPR, IK-CAPE, or BARIN models. The heat of vaporization can be calculated from the Watson/DIPPR/IK-CAPE model. The enthalpy departure is obtained from an equation-of-state.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
RSTATE †	—	2	—	—	—	—
TREFHL	$T_i^{ref,l}$	††	—	—	—	TEMPERATURE
DHLFRM	$H_i^{ref,l}$	O	—	—	—	MOLE-ENTHALPY
TCONHL	$T_i^{con,l}$	T	—	—	—	TEMPERATURE

† Enthalpy reference state, RSTATE=2 denotes saturated liquid as reference state.

†† For WILS-LR property method TREFHL defaults to 273.15K. For WILS-GLR property method, TREFHL defaults to 298.15 K.

Liquid heat capacity is required for all components.

Ideal Gas as Reference State

The saturated liquid enthalpy is calculated as follows:

$$H_i^{*,l} = H_i^{ref,ig} + \int_{T_i^{ref,ig}}^{T^{con,ig}} C_{p,i}^{*,ig} dT + \Delta H_{v,i}^*\left(T_i^{con,ig}, p_i^{*,l}\right) - \Delta_{vap} H_i^*\left(T_i^{con,ig}, p_i^{*,l}\right) + \int_{T_i^{con,ig}}^{T} C_{p,i}^{*,l} dT$$

Where:

$$H_i^{ref,ig}$$ = Reference state enthalpy for ideal gas at $T_i^{ref,ig}$

= Heat of formation of ideal gas at 298.15 K by default

$T_i^{ref,ig}$	=	Reference temperature corresponding to $H_i^{ref,ig}$. Defaults to 298.15 K
$T_i^{con,ig}$	=	The temperature at which one crosses from vapor state to liquid state. This is a user-defined temperature that defaults to the system temperature T. $T_i^{con,ig}$ may be selected such that heat of vaporization of component i at the temperature is most accurate.

The ideal gas enthalpy is calculated as follows:

$$H_i^{*,ig} = H_i^{ref,ig} + \int_{T_i^{ref,ig}}^{T} C_{p,i}^{*,ig} dT$$

The vapor enthalpy is calculated as follows:

$$H_i^{*,v} = H_i^{*,ig} + \Delta H_{v,i}(T,P)$$

The liquid heat capacity and the ideal gas heat capacity can be calculated from the ASPEN, DIPPR, IK-CAPE, or BARIN models. The heat of vaporization can be calculated from the Watson/DIPPR/IK-CAPE model. The enthalpy departure is obtained from an equation-of-state.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
RSTATE	—	1 or 2 †	—	—	—	—
TREFHI	$T_i^{ref,ig}$	††	—	—	—	TEMPERATURE
DHFORM	$H_i^{ref,ig}$	—	—	—	—	MOLE-ENTHALPY
TCONHI	$T_i^{con,l}$	T	—	—	—	TEMPERATURE

† Enthalpy reference state. RSTATE can be 1 (for ideal gas) or 2 (for liquid)

†† For components with TB < 298.15 K, RSTATE defaults to 1 (ideal gas). TREFHI defaults to 298.15 K.
For components with TB > 298.15 K, RSTATE defaults to 2 (liquid). TREFHL defaults to 298.15 K.

Helgeson Equations of State

The Helgeson equations of state for standard volume $\overline{V}^o$, heat capacity $\overline{C}_p^o$, entropy $\overline{S}^o$, enthalpy of formation $\Delta\overline{H}^o$, and Gibbs energy of formation $\Delta\overline{G}^o$ at infinite dilution in aqueous phase are:

$$\overline{V}^o = a_1 + a_2\left(\frac{1}{p+\psi}\right) + \left[a_3 + a_4\left(\frac{1}{p+\psi}\right)\right]\left(\frac{1}{T-\theta}\right) - \omega\ Q + \left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial p}\right)_T$$

$$\overline{C}_p^o = c_1 + \frac{c_2}{(T-\theta)^2} - \frac{2T}{(T-\theta)^3}\left[a_3(p-p_r) + a_4\ln\left(\frac{p+\psi}{p_r+\psi}\right)\right] + \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_p$$
$$- T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_p$$

$$\overline{S}^o = \overline{S}_{Tr\,Pr}^o + c_1\ln\left(\frac{T}{T_r}\right) - \frac{c_2}{\theta}\left[\frac{1}{T-\theta} - \frac{1}{T_r-\theta} + \frac{1}{\theta}\ln\left(\frac{T_r(T-\theta)}{T(T_r-\theta)}\right)\right]$$
$$+ \left(\frac{1}{T-\theta}\right)^2\left[a_3(p-p_r) + a_4\ln\left(\frac{p+\psi}{p_r+\psi}\right)\right] + \omega Y - \left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_p - \omega_{Tr\,Pr}Y_{Tr\,Pr}$$

$$\Delta\overline{H}^o = \Delta\overline{H}_f^o + c_1(T-T_r) - c_2\left(\frac{1}{T-\theta} - \frac{1}{T_r-\theta}\right) + a_1(p-p_r) + a_2\ln\left(\frac{p+\psi}{p_r+\psi}\right)$$
$$+ \left(\frac{2T-\theta}{(T-\theta)^2}\right)\left[a_3(p-p_r) + a_4\ln\left(\frac{p+\psi}{p_r+\psi}\right)\right] + \omega\left(\frac{1}{\varepsilon}-1\right) + \omega TY$$
$$- T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_p - \omega_{Tr\,Pr}\left(\frac{1}{\varepsilon_{Tr\,Pr}}-1\right) - \omega_{Tr\,Pr}T_rY_{Tr\,Pr}$$

$$\Delta\overline{G}^o = \Delta\overline{G}_f^o - \overline{S}_{Tr\,Pr}^o(T-T_r) - c_1\left[T\ln\left(\frac{T}{T_r}\right) - T + T_r\right] + a_1(p-p_r) + a_2\ln\left(\frac{p+\psi}{p_r+\psi}\right)$$
$$- c_2\left[\left(\frac{1}{T-\theta} - \frac{1}{T_r-\theta}\right)\left(\frac{\theta-T}{\theta}\right) - \frac{T}{\theta^2}\ln\left(\frac{T_r(T-\theta)}{T(T_r-\theta)}\right)\right]$$
$$+ \frac{1}{T-\theta}\left[a_3(p-p_r) + a_4\ln\left(\frac{p+\psi}{p_r+\psi}\right)\right] + \omega\left(\frac{1}{\varepsilon}-1\right)$$
$$- \omega_{Tr\,Pr}\left(\frac{1}{\varepsilon_{Tr\,Pr}}-1\right) + \omega_{Tr\,Pr}Y_{Tr\,Pr}(T-T_r)$$

Where:

$$Q = \frac{1}{\varepsilon}\left(\frac{\partial \ln\varepsilon}{\partial P}\right)_T$$

$$X = \frac{1}{\varepsilon}\left[\left(\frac{\partial^2 \ln\varepsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln\varepsilon}{\partial T}\right)_P^2\right]$$

$$Y = \frac{1}{\varepsilon}\left(\frac{\partial \ln\varepsilon}{\partial T}\right)_P$$

Where:

ψ	=	Pressure constant for a solvent (2600 bar for water)
θ	=	Temperature constant for a solvent (228 K for water)
ω	=	Born coefficient
ε	=	Dielectric constant of a solvent
T_r	=	Reference temperature (298.15 K)
P_r	=	Reference pressure (1 bar)

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
AHGPAR/1, . , 4	$a_1,...,a_4$	0	—	—	—	—
CHGPAR/1, . , 2	c_1, c_2	x	—	—	—	—
DHAQHG	$\Delta\overline{H}_f^o$	0	—	-0.5×10^{10}	0.5×10^{10}	MOLE-ENTHALPY
DGAQHG	$\Delta\overline{G}_f^o$	0	—	-0.5×10^{10}	0.5×10^{10}	MOLE-ENTHALPY
S25HG	$\overline{S}_{Tr\,Pr}^o$	0	—	-0.5×10^{10}	0.5×10^{10}	MOLE-ENTROPY
OMEGHG	$\omega_{Tr\,Pr}$	0	—	-0.5×10^{10}	0.5×10^{10}	MOLE-ENTHALPY

If pressure is under 200 bar, AHGPAR may not be required.

References

Tanger J.C. IV and H.C. Helgeson, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equation of state for the standard partial properties of ions and electrolytes, American Journal of Science, Vol. 288, (1988), p. 19-98.

Shock E.L. and H.C. Helgeson, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation

of state predictions to 5 kb and 1000 °C, Geochimica et Cosmochimica Acta, Vol. 52, p. 2009-2036.

Shock E.L. H.C. Helgeson and D.A. Sverjensky, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species, Geochimica et Cosmochimica Acta, Vol. 53, p. 2157-2183.

Transport Property Models

This section describes the transport property models available in the Aspen Physical Property System. The following table provides an overview of the available models. This table lists the Aspen Physical Property System model names, and their possible use in different phase types, for pure components and mixtures.

Transport Property Models

Viscosity models	Model name	Phase(s)	Pure	Mixture
Andrade/DIPPR/IK-CAPE	MUL0ANDR, MUL2ANDR	L	X	X
API Liquid Viscosity	MUL2API	L	—	X
Chapman-Enskog-Brokaw /DIPPR/IK-CAPE	MUV0CEB	V	X	—
Chapman-Enskog-Brokaw-Wilke Mixing Rule	MUV2BROK, MUV2WILK	V	—	X
Chung-Lee-Starling Low Pressure	MUL0CLSL, MUL2CLSL	V	X	X
Chung-Lee-Starling	MUV0CLS2, MUV0CLS2, MUL0CLS2, MUL2CLS2	V L	X	X
Dean-Stiel Pressure Correction	MUV0DSPC, MUV2DSPC	V	X	X
IAPS Viscosity	MUV0H2O	V	X	—
	MUL0H2O	L	X	—
Jones-Dole Electrolyte Correction	MUL2JONS	L	—	X
Letsou-Stiel	MUL0LEST, MUL2LEST	L	X	X
Lucas	MUV0LUC, MUV2LUC	V	X	X
TRAPP viscosity	MUL0TRAP, MUL2TRAP, MUV0TRAP, MUV2TRAP	VL	X	X

Thermal conductivity models	Model name	Phase(s)	Pure	Mixture
Chung-Lee-StarlingThermal Conductivtity	KV0CLS2, KV2CLS2, KL0CLS2, KL2CLS2	V L	X	X
IAPS Thermal Conductivity	KV0H2O	V	X	—
	KL0H2O	L	X	—
Li Mixing Rule	KL2LI	L	X	X
Riedel Electrolyte Correction	KL2RDL	L	—	X
Sato-Riedel/DIPPR/IK-CAPE	KL0SR, KL2SRVR	L	X	X
Stiel-Thodos/DIPPR/IK-CAPE	KV0STLP	V	X	—
Stiel-Thodos Pressure Correction	KV0STPC, KV2STPC	V	X	X
TRAPP Thermal Conductivity	KV0TRAP, KV2TRAP, KL0TRAP, KL2TRAP	V L	X	X
Vredeveld Mixing Rule	KL2SRVR	L	X	X
Diffusivity models	**Model name**	**Phase(s)**	**Pure**	**Mixture**
Chapman-Enskog-Wilke-Lee Binary	DV0CEWL	V	—	X
Chapman-Enskog-Wilke-Lee Mixture	DV1CEWL	V	—	X
Dawson-Khoury-Kobayashi Binary	DV1DKK	V	—	X
Dawson-Khoury-Kobayashi Mixture	DV1DKK	V	—	X
Nernst-Hartley Electrolytes	DL0NST, DL1NST	L	—	X
Wilke-Chang Binary	DL0WC2	L	—	X
Surface tension models	**Model name**	**Phase(s)**	**Pure**	**Mixture**
API Surface Tension	SIG2API	L	—	X
Hakim-Steinberg-Stiel/DIPPR /IK-CAPE	SIG0HSS, SIG2HSS	L	X	—
IAPS surface tension	SIG0H2O	L	X	—
Onsager-Samaras Electrolyte Correction	SIG2ONSG	L	—	X

Viscosity Models

The Aspen Physical Property System has 12 built-in viscosity models.

Model	Type
Andrade/DIPPR/IK-CAPE	Liquid
API liquid viscosity	Liquid
Chapman-Enskog-Brokaw/DIPPR/IK-CAPE	Low pressure vapor, pure components
Chapman-Enskog-Brokaw-Wilke Mixing Rule	Low pressure vapor, mixture
Chung-Lee-Starling Low Pressure	Low pressure vapor
Chung-Lee-Starling	Liquid or vapor
Dean-Stiel Pressure correction	Vapor
IAPS viscosity	Water or steam
Jones-Dole Electrolyte Correction	Electrolyte
Letsou-Stiel	High temperature liquid
Lucas	Vapor
TRAPP viscosity	Vapor or liquid

Andrade/DIPPR/IK-CAPE Liquid Viscosity

The liquid mixture viscosity is calculated by the equation:

$$\ln \eta^l = \sum_i x_i \ln \eta_i^{*,l} + \sum_i \sum_j \left(k_{ij} x_i x_j + m_{ij} x_i^2 x_j^2 \right)$$

Where:

$$k_{ij} \quad = \quad a_{ij} + \frac{b_{ij}}{T}$$

$$m_{ij} \quad = \quad c_{ij} + \frac{d_{ij}}{T}$$

The pure component liquid viscosity $\eta_i^{*,l}$ can be calculated by three models:

- Andrade
- DIPPR liquid viscosity
- IK-CAPE

The binary parameters *kij* and *mij* allow accurate representation of complex liquid mixture viscosity. Both binary parameters default to zero.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
ANDKIJ/1	a_{ij}	0	—	—	—	—
ANDKIJ/2	b_{ij}	0	—	—	—	—
ANDMIJ/1	c_{ij}	0	—	—	—	—
ANDMIJ/2	d_{ij}	0	—	—	—	—

Andrade Liquid Viscosity

The Andrade equation is:

$$\ln \eta_i^{*,l} = A_i + \frac{B_i}{T} + C_i \ln T \quad \text{for} \ \ T_l \leq T \leq T_h$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MULAND/1	A_i	—	X	—	—	VISCOSITY, TEMPERATURE
MULAND/2	B_i	—	X	—	—	TEMPERATURE
MULAND/3	C_i	—	X	—	—	TEMPERATURE
MULAND/4	T_l	0.0	X	—	—	TEMPERATURE
MULAND/5	T_h	500.0	X	—	—	TEMPERATURE

If elements 2 or 3 are non-zero, absolute temperature units are assumed for elements 1 to 3.

DIPPR Liquid Viscosity

The equation for the DIPPR liquid viscosity model is:

$$\ln \eta_i^{*,l} = C_{1i} + C_{2i}/T + C_{3i} \ln T + C_{4i} T^{C_{5i}} \quad \text{for} \ \ C_{6i} \leq T \leq C_{7i}$$

If the MULDIP parameters for a given component are available, the DIPPR equation is used instead of the Andrade model. The Andrade model is also used by PCES.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MULDIP/1	C_{1i}	—	X	—	—	VISCOSITY, TEMPERATURE
MULDIP/2,..., 5	$C_{2i},\ldots,C_{5i}$	0	X	—	—	TEMPERATURE
MULDIP/6	C_{6i}	0	X	—	—	TEMPERATURE
MULDIP/7	C_{7i}	1000	X	—	—	TEMPERATURE

If elements 3, 4, or 5 are non-zero, absolute temperature units are assumed for elements 1 to 5.

IK-CAPE Liquid Viscosity Model

The IK-CAPE liquid viscosity model includes both exponential and polynomial equations.

Exponential

$$\eta_i^{*,l} = C_{1i} \exp\left(\frac{C_{2i}}{T}\right) + C_{3i} \text{ for } C_{4i} \leq T \leq C_{5i}$$

If the parameter MULIKC is available, the Aspen Physical Property System uses the exponential IK-CAPE equation.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MULIKC/1	C_{1i}	—	X	—	—	VISCOSITY
MULIKC/2	C_{2i}	0	X	—	—	TEMPERATURE
MULIKC/3	C_{3i}	0	X	—	—	VISCOSITY
MULIKC/4	C_{4i}	0	X	—	—	TEMPERATURE
MULIKC/5	C_{5i}	1000	X	—	—	TEMPERATURE

If element 2 is non-zero, absolute temperature units are assumed for elements 1 to 3.

Polynomial

$$\eta_i^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

for $C_{11i} \leq T \leq C_{12i}$

If the parameter MULPO is available, the Aspen Physical Property System uses the polynomial equation.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MULPO/1	C_{1i}	—	X	—	—	VISCOSITY
MULPO/2,..., 10	$C_{2i},...,C_{10i}$	0	X	—	—	VISCOSITY, TEMPERATURE
MULPO/11	C_{11i}	0	X	—	—	TEMPERATURE
MULPO/12	C_{12i}	1000	X	—	—	TEMPERATURE

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, The Properties of Gases and Liquids, 4th ed., (New York: McGraw-Hill, 1987), p. 439.

API Liquid Viscosity

The liquid mixture viscosity is calculated using a combination of the API and Andrade/DIPPR equations. This model is recommended for petroleum and petrochemical applications. It is used in the CHAO-SEA, GRAYSON, LK-PLOCK, PENG-ROB, and RK-SOAVE option sets.

For pseudocomponents, the API model is used:

$$\eta^l = fcn\left(T, x, T_{bi}, API_i, V_m^l\right)$$

Where:

fcn = A correlation based on API Procedures and Figures 11A4.1, 11A4.2, and 11A4.3 (*API Technical Data Book*, *Petroleum Refining*, 4th edition)

V_m^l is obtained from the API liquid volume model.

For real components, the Andrade/DIPPR model is used.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TB	T_{bi}	—	—	4.0	2000.0	TEMPERATURE
API	API_i	—	—	-60.0	500.0	—

Chapman-Enskog-Brokaw/DIPPR/IK-CAPE

The pure component low pressure vapor viscosity $\eta_i^{*,v}$ ($p = 0$) can be calculated using three models:

- Chapman-Enskog
- DIPPR vapor viscosity
- IK-CAPE

Chapman-Enskog-Brokaw

The equation for the Chapman-Enskog model is:

$$\eta_i^{*,v}\left(p = 0\right) = 2.669 \times 10^{-26} \frac{\sqrt{M_i T}}{\sigma_i^2 \Omega_\eta}$$

Where:

$$\Omega_\eta = fcn\left(T, \varepsilon_i/k\right)$$

Polar parameter δ is used to determine whether to use the Stockmayer or Lennard-Jones potential parameters: ε/k (energy parameter) and σ (collision diameter). To calculate δ, the dipole moment p and either the Stockmayer parameters or the dipole moment T_b and V_{bm} are needed. The polarity correction is from Brokaw.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—
MUP	p_i	—	—	0.0	5x10-24	DIPOLEMOMENT
STKPAR/1	$(\varepsilon_i/k)^{ST}$	$fcn(T_{bi}, V_{bi}, p_i)$	—	X	—	TEMPERATURE
STKPAR/2	σ_i^{ST}	$fcn(T_{bi}, V_{bi}, p_i)$	X	—	—	LENGTH
LJPAR/1	$(\varepsilon_i/k)^{LJ}$	$fcn(T_{ci}, \omega_i)$	X	—	—	TEMPERATURE
LJPAR/2	σ_i^{LJ}	$fcn(T_{ci}, p_{ci}, \omega_i)$	X	—	—	LENGTH

DIPPR Vapor Viscosity

The equation for the DIPPR vapor viscosity model is:

$$\eta_i^{*,v}(p=0) = C_{1i}T^{C_{2i}}/\left(1 + C_{3i}/T + C_{4i}/T^2\right) \text{ for } C_{6i} \le T \le C_{7i}$$

If the MUVDIP parameters for a given component are available, the DIPPR equation is used instead of the Chapman-Enskog-Brokaw model. PCES uses the DIPPR vapor viscosity model.

Parameter Name/Element	Symbol	Default	MDS	LoweLimit	Upper Limit	Units
MUVDIP/1	C_{1i}	—	X	—	—	VISCOSITY
MUVDIP/2	C_{2i}	0	X	—	—	—
MUVDIP/3, 4	C_{3i}, C_{4i}	0	X	—	—	TEMPERATURE
MUVDIP/5	C_{5i}	0	X	—	—	—
MUVDIP/6	C_{6i}	0	X	—	—	TEMPERATURE
MUVDIP/7	C_{7i}	1000	X	—	—	TEMPERATURE

If elements 2, 3, or 4 are non-zero, absolute temperature units are assumed for elements 1 through 4.

IK-CAPE Vapor Viscosity

The IK-CAPE vapor viscosity model includes both the Sutherland equation and the polynomial equation.

Sutherland Equation

$$\eta_i^{*,v}(p=0) = C_{1i}T^{0.5}/(1 + C_{2i}/T) \text{ for } C_{3i} \le T \le C_{4i}$$

If the parameter MUVSUT is available, the Aspen Physical Property System uses the Sutherland equation.

Parameter Name/Element	Symbol	Default MDS	Lower Limit	Upper Limit	Units
MUVSUT/1	C_{1i}	—	X	—	—	VISCOSITY
MUVSUT/2	C_{2i}	0	X	—	—	TEMPERATURE
MUVSUT/3	C_{3i}	0	X	—	—	TEMPERATURE
MUVSUT/4	C_{4i}	1000	X	—	—	TEMPERATURE

If element 2 is non-zero, absolute temperature units are assumed for elements 1 to 2.

Polynomial

$$\eta_i^{*,v}(p=0) = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

for $C_{11i} \leq T \leq C_{12i}$

If the parameter MUVPO is available, the Aspen Physical Property System uses the polynomial equation.

Parameter Name/Element	Symbol	Default MDS	Lower Limit	Upper Limit	Units
MUVPO/1	C_{1i}	—	X	—	—	VISCOSITY
MUVPO/2,..., 10	$C_{2i},...,C_{10i}$	0	X	—	—	VISCOSITY, TEMPERATURE
MUVPO/11	C_{11i}	0	X	—	—	TEMPERATURE
MUVPO/12	C_{12i}	1000	X	—	—	TEMPERATURE

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling. *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 392.

Chapman-Enskog-Brokaw-Wilke Mixing Rule

The low pressure vapor mixture viscosity is calculated by the Wilke approximation of the Chapman-Enskog equation:

$$\eta^v(p=0) = \Sigma_i \frac{y_i \eta_i^{*,v}(p=0)}{\sum_j y_j \Phi_{ij}}$$

For Φ_{ij}, the formulation by Brokaw is used:

$$\Phi_{ij} = \left[\frac{\eta_i^{*,v}(p=0)}{\eta_j^{*,v}(p=0)} \right]^{1/2} S_{ij} A_{ij}$$

Where:

$$A_{ij} = fcn(M_i, M_j)$$, and the correction factor for polar gases

$$Sij = fcn\left(\delta, (\varepsilon/k)^{ST}, T\right)$$

Polar parameter δ is used to determine whether to use the Stockmayer or Lennard-Jones potential parameters: ε/k (energy parameter) and σ (collision diameter). To calculate δ, the dipole moment p, and either the Stockmayer parameters or T_b and V_{bm} are needed.

The pure component vapor viscosity $\eta_i^{*,v}$ ($p = 0$) can be calculated using the Chapman- Enskog-Brokaw/DIPPR (or another) low pressure vapor viscosity model.

Ensure that you supply parameters for $\eta_i^{*,v}$ ($p = 0$).

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—
MUP	p_i	—	—	0.0	5x10-24	DIPOLEMOMENT
STKPAR/1	$(\varepsilon_i/k)^{ST}$	$fcn(T_{bi}, V_{bi}, p_i)$	—	X	—	TEMPERATURE
STKPAR/2	σ_i^{ST}	$fcn(T_{bi}, V_{bi}, p_i)$	X	—	—	LENGTH

References

R.C. Reid, J.M. Prausnitz, and T.K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., (New York: McGraw-Hill, 1977), pp. 410–416.

Chung-Lee-Starling Low-Pressure Vapor Viscosity

The low-pressure vapor viscosity by Chung, Lee, and Starling is:

$$\eta^v(p = 0) = \frac{0.40785(MT)^{1/2} F_C}{V_{cm}^{2/3} \Omega_\eta}$$

Where the viscosity collision integral is:

$$\Omega_\eta = fcn(T_r)$$

The shape and polarity correction is:

$$F_c = fcn(\Omega, p_r, \kappa')$$

The parameter p_r is the reduced dipolemoment:

$$p_r = 4.152 \frac{p}{\left(V_{cm} T_c^{1/2}\right)}$$

The polar parameter κ' is tabulated for certain alcohols and carboxylic acids. The previous equations can be used for mixtures when applying these mixing rules:

$$V_{cm} = \sum_i \sum_j y_i y_j V_{cij}$$

$$T_c = \frac{\sum_i \sum_j y_i y_j T_{cij} V_{cij}}{V_{cm}}$$

$$M = \left[\frac{\sum_i \sum_j x_i x_j T_{cij} V_{cij}^{2/3} M_{ij}}{T_c V_{cm}^{2/3}} \right]^2$$

$$\omega = \frac{\sum_i \sum_j x_i x_j \omega_{ij} V_{cij}}{V_{cm}}$$

$$p_r = \frac{131.3 p}{V_{cm} T_c^{1/2}}$$

$$p^4 = \frac{\sum_i \sum_j x_i x_j p_i^2 p_j^2 V_c}{V_{cij}}$$

$$\kappa = \sum_i \sum_j x_i x_j \kappa_{ij}$$

Where:

V_{cij} $=$ $\left(1 - \xi_{ij}\right)\left(V_{ci} V_{cj}\right) \frac{1}{2}$

ξ_{ij} $=$ 0 (in almost all cases)

T_{cij} $=$ $\left(1 - \zeta_{ij}\right)\left(T_{ci} T_{cj}\right)^{1/2}$

ζ_{ij} $=$ 0 (in almost all cases)

ω_{ij} $=$ $\dfrac{\left(\omega_i + \omega_j\right)}{2}$

M_{ij} $=$ $\left[\dfrac{2 M_i M_j}{\left(M_i + M_j\right)} \right]^{1/2}$

$$\kappa_{ij} = \left(\kappa_i \kappa_j\right)^{1/2}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCCLS	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
VCCLS	V_{ci}	VC	x	0.001	3.5	MOLE-VOLUME
MW	M_i	—	—	1.0	5000.0	—
MUP	p_i	—	—	0.0	5×10^{-24}	DIPOLEMOMENT
OMGCLS	ω_i	OMEGA	x	-0.5	2.0	—
CLSK	κ_i	0.0	x	0.0	0.5	—
CLSKV	ξ_{ij}	0.0	x	-0.5	-0.5	—
CLSKT	ζ_{ij}	0.0	x	-0.5	0.5	—

The model specific parameters also affect the Chung-Lee-Starling Viscosity and the Chung-Lee-Starling Thermal Conductivity models.

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 396, p. 413.

Chung-Lee-Starling Viscosity

The Chung-Lee-Starling viscosity equation for vapor and liquid, high and low pressure is:

$$\eta^v = \frac{40.785 \left(MT\right)^{1/2} F_C}{V_{cm}^{2/3} \Omega_\eta} f_1 + \frac{36.344 \left(MT_c\right)^{1/2}}{V_{cm}^{2/3}} f_2$$

With:

$$f_1 = fcn\left(\rho_m, V_{cm}, \omega, p_r, \kappa\right)$$

$$f_2 = fcn\left(\omega, p_r, \kappa\right)$$

$$F_2 = fcn\left(\omega, p_r, \kappa\right)$$

The molar density can be calculated using an equation-of-state model (for example, the Benedict-Webb-Rubin). The parameter p_r is the reduced dipolemoment:

$$p_r = 4.152 \frac{p}{\left(V_{cm} T_c^{1/2}\right)}$$

The polar parameter κ is tabulated for certain alcohols and carboxylic acids.

For low pressures, f_1 is reduced to 1.0 and f_2 becomes negligible. The equation reduces to the low pressure vapor viscosity model by Chung-Lee and Starling.

The previous equations can be used for mixtures when applying these mixing rules:

$$V_{cm} = \sum_i \sum_j y_i y_j V_{cij}$$

$$T_c = \frac{\sum_i \sum_j y_i y_j T_{cij} V_{cij}}{V_{cm}}$$

$$M = \left[\frac{\sum_i \sum_j x_i x_j T_{cij} V_{cij}^{2/3} M_{ij}}{T_c V_{cm}^{2/3}} \right]^2$$

$$\omega = \frac{\sum_i \sum_j x_i x_j \omega_{ij} V_{cij}}{V_{cm}}$$

$$p_r = \frac{131.3 p}{V_{cm} T_c^{1/2}}$$

$$p^4 = \frac{\sum_i \sum_j x_i x_j p_i^2 p_j^2 V_c}{V_{cij}}$$

$$\kappa = \sum_i \sum_j x_i x_j \kappa_{ij}$$

Where:

$$V_{cij} \quad = \quad \left(1 - \xi_{ij}\right)\left(V_{ci} V_{cj}\right)^{1/2}$$

$$\xi_{ij} \quad = \quad 0 \text{ (in almost all cases)}$$

$$T_{cij} \quad = \quad \left(1 - \zeta_{ij}\right)\left(T_{ci} T_{cj}\right)^{1/2}$$

$$\zeta_{ij} \quad = \quad 0 \text{ (in almost all cases)}$$

$$\omega_{ij} \quad = \quad \frac{\left(\omega_i + \omega_j\right)}{2}$$

$$M_{ij} \quad = \quad \left[\frac{2 M_i M_j}{\left(M_i + M_j\right)} \right]^{1/2}$$

$$\kappa_{ij} = \left(\kappa_i \kappa_j\right)^{1/2}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCCLS	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
VCCLS	V_{ci}	VC	x	0.001	3.5	MOLE-VOLUME
MW	M_i	—	—	1.0	5000.0	—
MUP	p_i	—	—	0.0	5×10^{-24}	DIPOLEMOMENT
OMGCLS	ω_i	OMEGA	x	-0.5	2.0	—
CLSK	κ_i	0.0	x	0.0	0.5	—
CLSKV	ξ_{ij}	0.0	x	-0.5	-0.5	—
CLSKT	ζ_{ij}	0.0	x	-0.5	0.5	—

The model specific parameters affect the results of the Chung-Lee-Starling Thermal Conductivity and Low Pressure Viscosity models as well.

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 427.

Dean-Stiel Pressure Correction

The pressure correction to low pressure vapor viscosity or the residual vapor viscosity by Dean and Stiel is:

$$\eta^v(p) - \eta^v(p=0) = \frac{1.08}{\xi}\left[10^{1.439\rho_m} - 10^{\left(-1.111\rho_{rm}^{1.858}\right)}\right]$$

Where $\eta^v(p=0)$ is obtained from a low pressure viscosity model (for example, Chapman-Enskog-Brokaw). The dimensionless-making factor ξ is:

$$\xi = N_A^2 \frac{T_c^{1/6}}{M^{1/2} p_c^{2/3}}$$

$$T_c = \sum_i y_i T_{ci}$$

$$M = \sum_i y_i M_i$$

$$p_c = \frac{Z_{cm} R T_c}{V_{cm}}$$

$$V_{cm} \quad = \quad \sum_i y_i V_{ci}$$

$$Z_{cm} \quad = \quad \sum_i y_i Z_{ci}$$

$$\rho_{rm} \quad = \quad \frac{V_{cm}}{V_m^v}$$

The parameter V_m^v is obtained from Redlich-Kwong equation-of-state.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—
VC	V_{ci}	—	—	0.001	3.5	MOLE-VOLUME

IAPS Viscosity for Water   The IAPS viscosity models, developed by the International Association for Properties of Steam, calculate vapor and liquid viscosity for water and steam. These models are used in option sets STEAMNBS and STEAM-TA.

The general form of the equation for the IAPS viscosity models is:

$$\eta_w = fcn(T, p)$$

Where:

fcn = Correlation developed by IAPS

The models are only applicable to water. There are no parameters required for the models.

Jones-Dole Electrolyte Correction   The Jones-Dole model calculates the correction to the liquid mixture viscosity of a solvent mixture, due to the presence of electrolytes:

$$\eta^l = \eta_{solv}\left(1 + \sum_{ca} \Delta\eta_{ca}^l\right)$$

Where:

η_{solv} = Viscosity of the liquid solvent mixture, calculated by the Andrade/DIPPR model

$\Delta\eta_{ca}^l$ = Contribution to the viscosity correction due to apparent electrolyte ca

The parameter $\Delta\eta_{ca}^l$ can be calculated by three different equations.

If these parameters are available	Use this equation
IONMOB and IONMUB	Dole-Jones
IONMUB	Breslau-Miller
—	Carbonell

Jones-Dole

The Jones-Dole equation is:

$$\Delta\eta_{ca}^l = A_{ca}\sqrt{c_{ca}^a} + B_{ca}c_{ca}^a \tag{1}$$

Where:

$$c_{ca}^a = \frac{x_{ca}^a}{V_m^l} \quad = \quad \text{Concentration of apparent electrolyte } ca \tag{2}$$

$$x_{ca}^a \quad\quad = \quad \text{Mole fraction of apparent electrolyte } ca \tag{3}$$

$$A_{ca} \quad\quad = \quad \frac{1.45}{\eta_{solv}^l (2\varepsilon T)^{1/2}}\left[\frac{L_c + L_a}{4L_c L_a} - \frac{L_c - L_a}{\left(3 + \sqrt{2}\,L_c L_a\left(L_c + L_a\right)\right)}\right] \tag{4}$$

$$L_a \quad\quad = \quad l_{a,1} + l_{a,2}T \tag{5}$$

$$L_c \quad\quad = \quad l_{c,1} + l_{c,2}T \tag{6}$$

$$B_{ca} \quad\quad = \quad \left(b_{c,1} + b_{c,2}T\right) + \left(b_{a,1} + b_{a,2}T\right) \tag{7}$$

Breslau-Miller

The Breslau-Miller equation is:

$$\Delta\eta_{ca}^l = 2.5V_e c_{ca}^a + 10.05V_e\left(c_{ca}^a\right)^2 \tag{8}$$

Where the effective volume *Vc* is given by:

$$V_e = \frac{\left(B_{ca} - 0.002\right)}{2.60} \quad \text{for salts involving univalent ions} \tag{9}$$

$$V_e = \frac{\left(B_{ca} - 0.011\right)}{5.06} \quad \text{for other salts} \tag{9a}$$

Carbonell

The Carbonell equation is:

$$\Delta\eta_{ca}^l = \exp\left[0.48193\left(\sum_k M_k x_k^a\right)\frac{c_{ca}^a}{T}\right] - 1.0 \tag{10}$$

Where:

M_k = Molecular weight of an apparent electrolyte component k

You must provide parameters for the Andrade model, used for the calculation of the liquid mixture viscosity of the solvent mixture.

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
CHARGE	z	0.0	—	—	—
MW	M	—	1.0	5000.0	—
IONMOB/1	I_1	—	—	—	AREA, MOLES
IONMOB/2	I_2	0.0	—	—	AREA, MOLES, TEMPERATURE
IONMUB/1	b_1	—	—	—	MOLE-VOLUME
IONMUB/2	b_2	0,0	—	—	MOLE-VOLUME, TEMPERATURE

References

A. L. Horvath, *Handbook of Aqueous Elecrolyte Solutions*, (Chichester: Ellis Horwood, 1985).

Letsou-Stiel

The Letsou-Stiel model calculates liquid viscosity at high temperatures for $0.76 \le T_r \le 0.98$. This model is used in PCES.

The general form for the model is:

$$\eta'\varepsilon = \left(\eta'\varepsilon\right)^0 + \omega\left(\eta'\varepsilon\right)^1$$

Where:

$\left(\eta'\varepsilon\right)^0$ = $fcn\left(T, x_i, T_{ci}\right)$

$\left(\eta'\varepsilon\right)^1$ = $fcn\left(T, x_i, T_{ci}\right)$

ε = $fcn\left(x_i, M_i, T_{ci}, p_{ci}, \omega_i\right)$

ω = $\sum_i x_i \omega_i$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
PC	p_{ci}	—	—	10^5	10^5	PRESSURE
OMEGA	ω_i	—	—	-0.5	2.0	—

References

R.C. Reid, J.M. Pransnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 471.

Lucas Vapor Viscosity

The equation for the Lucas vapor viscosity model is:

$$\eta^v = \left(\eta^v(p=0)\xi\right)\frac{YF_pF_Q}{\xi}$$

Where the dimensionless low pressure viscosity is given by:

$$\left(\eta^v(p=0)\xi\right) = fcn(T_r)F_P(p=0)F_Q(p=0)$$

The dimensionless-making group is:

$$\xi = N_A^2 \frac{T_c^{1/6}}{M^{1/2}p_c^{2/3}}$$

The pressure correction factor Y is:

$$Y = fcn(p_r, T_r)$$

The polar and quantum correction factors at high and low pressure are:

$$F_P \quad = \quad fcn\left(Y, F_P(p=0)\right)$$

$$F_Q \quad = \quad fcn\left(Y, F_Q(p=0)\right)$$

$$F_{Pi}(p=0) \quad = \quad fcn(T_{ri}, p_{ci}, Z_{ci}, \boldsymbol{p}_i)$$

$$F_{Qi}(p=0) \quad = \quad fcn(T_{ri})\text{, but is only nonunity for the quantum gates } i = H_2, E_2 \text{ and } He.$$

The Lucas mixing rules are:

$$T_c \quad = \quad \sum_i y_i T_{ci}$$

$$p_c \quad = \quad RT_c \frac{\sum_i y_i Z_{ci}}{\sum_i y_i V_{ci}},$$

$$V_{ci} = \frac{RZ_{ci}T_{ci}}{p_{ci}}$$

$$M \quad = \quad \sum_i y_i M_i$$

$$F_P(p=0) \quad = \quad \sum y_i F_{Pi}(p=0)$$

$$F_Q(p=0) \quad = \quad A\sum y_i F_{Qi}(p=0)$$

Where *A* differs from unity only for certain mixtures.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCLUC	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCLUC	p_{ci}	PC	x	10^5	10^8	PRESSURE
ZCLUC	Z_{ci}	ZC	x	0.1	0.5	—
MW	M_i	—	—	1.0	5000.0	—
MUP	$\boldsymbol{p}_i$	—	—	0.0	5×10^{-24}	DIPOLEMOMENT

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 421, 431.

TRAPP Viscosity Model The general form for the TRAPP viscosity model is:

$$\eta = fcn\left(t, p, \overline{x}, M_i, T_{ci}, p_{ci}, V_{ci}, Z_{ci}, \omega_i\right)$$

Where:

The parameter $\overline{x}$ is the mole fraction vector; *fcn* is a corresponding states correlation based on the model for vapor and liquid viscosity TRAPP, by the National Bureau of Standards (NBS, currently NIST) . The model can be used for both pure components and mixtures. The model should be used for nonpolar components only.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—
TCTRAP	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCTRAP	p_{ci}	PC	x	10^5	10^8	PRESSURE
VCTRAP	V_{ci}	VC	x	0.001	3.5	MOLE-VOLUME
ZCTRAP	Z_{ci}	ZC	x	0.1	1.0	—
OMGRAP	ω_i	OMEGA	x	-0.5	3.0	—

References

J.F. Ely and H.J.M. Hanley, "Prediction of Transport Properties. 1. Viscosities of Fluids and Mixtures," *Ind. Eng. Chem. Fundam.*, Vol. 20, (1981), pp. 323–332.

Thermal Conductivity Models

The Aspen Physical Property System has eight built-in thermal conductivity models. This section describes the thermal conductivity models available.

Model	Type
Chung-Lee-Starling	Vapor or liquid
IAPS	Water or stream
Li Mixing Rule	Liquid mixture
Riedel Electrolyte Correction	Electrolyte
Sato-Riedel/DIPPR/IK-CAPE	Liquid
Stiel-Thodos/DIPPR/IK-CAPE	Low pressure vapor
Stiel-Thodos Pressure Correction	Vapor
TRAPP Thermal Conductivity	Vapor or liquid
Vredeveld Mixing Rule	Liquid mixture
Wassiljewa-Mason-Saxena Mixing Rule	Low pressure vapor

Chung-Lee-Starling Thermal Conductivity

The main equation for the Chung-Lee-Starling thermal conductivity model is:

$$\lambda = \frac{31.2\eta(p=0)\Psi}{M}f_1 + f_2$$

Where:

$$f_1 \quad = \quad fcn(\rho_m, \omega, \pmb{p}_r, \kappa)$$

$$f_2 \quad = \quad fcn(T_c, M, V_{cm}, \rho_{rm}, \omega, \pmb{p}_r, \kappa)$$

$$\Psi \quad = \quad fcn(C_v, \omega, T_r)$$

$\eta(p=0)$ can be calcuated by the low pressure Chung-Lee-Starling model. The molar density can be calculated using an equation-of-state model (for example, the Benedict-Webb-Rubin equation-of-state). The parameter $\pmb{p}_r$ is the reduced dipolemoment:

$$\pmb{p}_r = 4.152\frac{\pmb{p}}{\left(V_{cm}T_c^{\frac{1}{2}}\right)}$$

The polar parameter κ is tabulated for certain alcohols and carboxylic acids.

For low pressures, f_1 is reduced to 1.0 and f_2 is reduced to zero. This gives the Chung-Lee-Starling expression for thermal conductivity of low pressure gases.

The same expressions are used for mixtures. The mixture expression for $\eta(p=0)$ must be used. (See Chung-Lee-Starling Low-Pressure Vapor Viscosity.)

$$C_v = \sum_i x_i C_{v,i}$$

$$M = \left[\frac{\sum_i \sum_j x_i x_j T_{cij} V_{cij}^{2/3} M_{ij}}{T_c V_{cm}^{2/3}} \right]^2$$

$$\omega = \frac{\sum_i \sum_j x_i x_j \omega_{ij} V_{cij}}{V_{cm}}$$

$$p_r = \frac{131.3p}{V_{cm} T_c^{1/2}}$$

$$p^4 = \frac{\sum_i \sum_j x_i x_j p_i^2 p_j^2 V_c}{V_{cij}}$$

$$\kappa = \sum_i \sum_j x_i x_j \kappa_{ij}$$

Where:

V_{cij}	=	$\left(1 - \xi_{ij}\right)\left(V_{ci} V_{cj}\right) \tfrac{1}{2}$
ξ_{ij}	=	0 (in almost all cases)
T_{cij}	=	$\left(1 - \zeta_{ij}\right)\left(T_{ci} T_{cj}\right)^{1/2}$
ζ_{ij}	=	0 (in almost all cases)
ω_{ij}	=	$\dfrac{\left(\omega_i + \omega_j\right)}{2}$
M_{ij}	=	$\left[\dfrac{2 M_i M_j}{\left(M_i + M_j\right)} \right]^{1/2}$
κ_{ij}	=	$\left(\kappa_i \kappa_j\right)^{1/2}$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TCCLS	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
VCCLS	V_{ci}	VC	x	0.001	3.5	MOLE-VOLUME
MW	M_i	—	—	1.0	5000.0	—
MUP	p_i	—	—	0.0	5×10^{-24}	DIPOLEMOMENT
OMGCLS	ω_i	OMEGA	x	-0.5	2.0	—
CLSK	κ_i	0.0	x	0.0	0.5	—
CLSKV	ξ_{ij}	0.0	x	-0.5	-0.5	—
CLSKT	ζ_{ij}	0.0	x	-0.5	0.5	—

The model-specific parameters also affect the results of the Chung-Lee-Starling viscosity models.

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, The Properties of Gases and Liquids, 4th ed., (New York: McGraw-Hill, 1987), p. 505, 523.

IAPS Thermal Conductivity for Water

The IAPS thermal conductivity models were developed by the International Association for Properties of Steam. These models can calculate vapor and liquid thermal conductivity for water and steam. They are used in option sets STEAMNBS and STEAM-TA.

The general form of the equation for the IAPS thermal conductivity models is:

$$\lambda_w = fcn(T, p)$$

Where:

fcn	=	Correlation developed by IAPS

The models are only applicable to water. No parameters are required.

Li Mixing Rule

Liquid mixture thermal conductivity is calculated using Li equation (Reid et.al., 1987):

$$\lambda^l = \sum_i \sum_j \Phi_i \Phi_j \lambda_{ij}$$

Where:

$$\lambda_{ij} = 2 \left[\left(\lambda_i^{*,l} \right)^{-1} + \left(\lambda_j^{*,l} \right)^{-1} \right]^{-1}$$

$$\Phi_i = \frac{x_i V_i^{*,l}}{\sum_j x_i V_j^{*,l}}$$

The pure component liquid molar volume $V_i^{*,l}$ is calculated from the Rackett model.

The pure component liquid thermal conductivity $\lambda_i^{*,l}$ can be calculated by three models:

- Sato-Riedel
- DIPPR
- IK-CAPE

See the Sato-Riedel/DIPPR/IK-CAPE model for descriptions.

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 550.

Riedel Electrolyte Correction

The Riedel model can calculate the correction to the liquid mixture thermal conductivity of a solvent mixture, due to the presence of electrolytes:

$$\lambda^l(T) = \left[\lambda_{solv}^l(T = 293) + \sum_{ca}(a_c + a_a)\frac{x_{ca}^a}{V_m^l} \right] \frac{\lambda_{solv}^l(T)}{\lambda_{solv}^l(T = 293)}$$

Where:

λ_{solv}^l	=	Thermal conductivity of the liquid solvent mixture, calculated by the Sato-Riedel model
x_{ca}^a	=	Mole fraction of the apparent electrolyte *ca*
a_c, a_a	=	Reidel ionic coefficient
V_m^l	=	Apparent molar volume computed by the Clarke density model

Apparent electrolyte mole fractions are computed from the true ion mole-fractions and ionic charge number. They can also be computed if you use the apparent component approach. A more detailed discussion of this method is found in Chapter 5.

You must provide parameters for the Sato-Riedel model. This model is used for the calculation of the thermal conductivity of solvent mixtures.

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
CHARGE	z	0.0	—	—	—
IONRDL	a	0.0	—	—	THERMAL CONDUCTIVITY, MOLE-VOLUME

Sato-Riedel/DIPPR/IK-CAPE Liquid Thermal Conductivity

The pure component liquid thermal conductivity can be calculated by three models:

- Sato-Riedel
- DIPPR liquid thermal conductivity
- IK-CAPE

Sato-Riedel

The Sato-Riedel equation is (Reid et al., 1987):

$$\lambda_i^{*,l} = \frac{1.1053152}{M_i^{\frac{1}{2}}}\left(\frac{3 + 20(1 - T_{ri})^{\frac{2}{3}}}{3 + 20(1 - T_{bri})^{\frac{2}{3}}}\right)$$

Where:

$$T_{bri} = T_{bi}/T_{ci}$$

$$T_{ri} = T/T_{ci}$$

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
TB	T_{bi}	—	—	4.0	2000.0	TEMPERATURE

DIPPR Liquid Thermal Conductivity

The DIPPR equation is:

$$\lambda_i^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 \ \ \text{for} \ \ C_{6i} \le T \le C_{7i}$$

Linear extrapolation of $\lambda^{*,l}$ versus T occurs outside of bounds.

If the KLDIP parameters for a given component are available, the DIPPR model is used instead of the Sato-Riedel model. The DIPPR model is also used by PCES.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
KLDIP/1	C_{1i}	—	x	—	—	THERMAL-CONDUCTIVITY, TEMPERATURE
KLDIP/2, … , 5	$C_{2i},…,C_{5i}$	0	x	—	—	THERMAL-CONDUCTIVITY, TEMPERATURE
KLDIP/6	C_{6i}	0	x	—	—	TEMPERATURE
KLDIP/7	C_{7i}	1000	x	—	—	TEMPERATURE

IK-CAPE

The IK-CAPE equation is a polynomial containing 10 terms. If the parameter KLPO is available, the Aspen Physical Property System uses the IK-CAPE equation.

$$\lambda_i^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

for $C_{11i} \leq T \leq C_{12i}$

Linear extrapolation of $\lambda^{*,l}$ versus T occurs outside of bounds.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
KLPO/1	C_{1i}	—	x	—	—	THERMAL-CONDUCTIVITY
KLPO/2, … , 10	$C_{2i},...,C_{10i}$	0	x	—	—	THERMAL-CONDUCTIVITY, TEMPERATURE
KLPO/11	C_{11i}	0	x	—	—	TEMPERATURE
KLPO/12	C_{12i}	1000	x	—	—	TEMPERATURE

References

R.C. Reid, J.M. Prausnitz, and T.K. Sherwood, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1977), p. 533.

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 550.

Vredeveld Mixing Rule

Liquid mixture thermal conductivity is calculated using the Vredeveld equation (Reid et al., 1977):

$$\lambda^l = \left[\sum_i \left(\frac{\left(\lambda_i^{*,l}\right)^2}{x_i M_i} \right) \sum_j x_j M_j \right]^{\frac{1}{2}}$$

Pure component liquid thermal conductivity $\lambda_i^{*,l}$ can be calculated by two equations:

- Sato-Riedel
- DIPPR
- IK-CAPE

See the Sato-Riedel/DIPPR/IK-CAPE model for descriptions.

R.C. Reid, J.M. Prausnitz, and T.K. Sherwood, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1977), p. 533.

Stiel-Thodos/DIPPR/IK-CAPE Vapor Thermal Conductivity

The pure component vapor thermal conductivity for low pressure gasses can be calculated by three models:

- Stiel-Thodos
- DIPPR vapor thermal conductivity
- IK-CAPE polynomial

Stiel-Thodos

The Stiel-Thodos equation is:

$$\lambda_i^{*,v} = \eta_i^{*,v}\left(1.15\left(C_{pi}^{*,ig} - R\right) + 1.69 \times 10^4\right)\Big/ M_i$$

Where:

$\eta_i^{*,v}(p = 0)$ can be obtained from the Chapman-Enskog-Brokaw model.

$C_{pi}^{*,ig}$ is obtained from the Ideal Gas Heat Capacity model.

R is the universal gas constant.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—

DIPPR Vapor Thermal Conductivity

The DIPPR equation for vapor thermal conductivity is:

$$\lambda_i^{*,l} = C_{1i}T^{C_{2i}}\Big/\left(1 + C_{3i}/T + C_{4i}T^2\right) \text{ for } C_{6i} \leq T \leq C_{7i}$$

Linear extrapolation of $\lambda_i^{*,v}$ versus T occurs outside of bounds.

If the KVDIP parameters for a given component are available, the DIPPR equation is used instead of the Stiel-Thodos equation. The DIPPR equation is also used in PCES.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
KVDIP/1	C_{1i}	—	x	—	—	THERMAL CONDUCTIVITY
KVDIP/2	C_{2i}	0	x	—	—	—
KVDIP/3, 4	C_{3i}, C_{4i}	0	x	—	—	TEMPERATURE
KVDIP/5	—	0	x	—	—	—
KVDIP/6	C_{6i}	0	x	—	—	TEMPERATURE
KVDIP/7	C_{7i}	1000	x	—	—	TEMPERATURE

IK-CAPE Polynomial

$$\lambda_i^{*,v} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

for $C_{11i} \leq T \leq C_{12i}$

Linear extrapolation of $\lambda^{*,v}$ versus T occurs outside of bounds. If the parameter KVPO is available, the Aspen Physical Property System uses the IK-CAPE equation.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
KVPO/1	C_{1i}	—	x	—	—	THERMAL-CONDUCTIVITY
KVPO/2, … , 10	$C_{2i}, ..., C_{10i}$	0	x	—	—	THERMAL-CONDUCTIVITY, TEMPERATURE
KVPO/11	C_{11i}	0	x	—	—	TEMPERATURE
KVPO/12	C_{12i}	1000	x	—	—	TEMPERATURE

References

R.C. Reid, J.M. Praunitz, and B.E. Poling, *The Properties of Gases and Liquid*, 4th ed., (New York: McGraw-Hill, 1987), p. 494.

If elements 2, 3, or 4 are non-zero, absolute temperature units are assumed for elements 1 through 4.

Stiel-Thodos Pressure Correction Model

The pressure correction to a pure component or mixture thermal conductivity at low pressure is given by:

$$\lambda^v = fcn\left(\lambda^n(p=0), \rho_{rm}, y_i, M_i, T_{ci}, V_{ci}, Z_{ci}\right)$$

Where:

$$\rho_{rm} = \sum_i y_i \frac{V_{ci}}{V_m^v}$$

The parameter V_m^v can be obtained from Redlich-Kwong.

$\lambda^v(p=0)$ can be obtained from the low pressure Stiel-Thodos Thermal Conductivity model (Stiel-Thodos/DIPPR).

This model should not be used for polar substances, hydrogen, or helium.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—
TC	T_{ci}	—	—	5.0	2000.0	TEMPERATURE
PC	—	—	—	105	108	PRESSURE
VC	V_{ci}	—	—	0.001	3.5	MOLE-VOLUME
ZC	Z_{ci}	—	—	0.1	0.5	—

References

R.C. Reid, J.M. Praunitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 521.

TRAPP Thermal Conductivity Model

The general form for the TRAPP thermal conductivity model is:

$$\lambda = fcn\left(T, P, \bar{x}, M_i, T_{ci}, p_{ci}, V_{ci}, Z_{ci}, \omega_i, C_{p_i}^{*,ig}\right)$$

Where:

$\bar{x}$	=	Mole fraction vector
$C_{p_i}^{*,ig}$	=	Ideal gas heat capacity calculated using the Aspen Physical Property System or DIPPR ideal gas heat capacity equations
fcn	=	Corresponding states correlation based on the model for vapor and liquid thermal conductivity made by the National Bureau of standards (NBS, currently NIST)

The model can be used for both pure components and mixtures. The model should be used for nonpolar components only.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—
TCTRAP	T_{ci}	TC	x	5.0	2000.0	TEMPERATURE
PCTRAP	p_{ci}	PC	x	105	108	PRESSURE
VCTRAP	V_{ci}	VC	x	0.001	3.5	MOLE-VOLUME
ZCTRAP	Z_{ci}	ZC	x	0.1	1.0	—
OMGRAP	ω_i	OMEGA	x	-0.5	3.0	—

References

J.F. Ely and H.J. M. Hanley, "Prediction of Transport Properties. 2. Thermal Conductivity of Pure Fluids and Mixtures," *Ind. Eng. Chem. Fundam.*, Vol. 22, (1983), pp. 90–97.

Wassiljewa-Mason-Saxena Mixing Rule

The vapor mixture thermal conductivity at low pressures is calculated from the pure component values, using the Wassiljewa-Mason-Saxena equation:

$$\lambda^v(p=0) = \sum_i \frac{y_i \lambda_i^{*,v}(p=0)}{\sum_j y_j A_{ij}}$$

$$A_{ij} = \left[1 + \left[\frac{n_i^{*,v}(p=0)}{n_j^{*,v}(p=0)} \right]^{\frac{1}{2}} \left(M_j / M_i \right)^{\frac{1}{4}} \right]^{\frac{1}{2}} \Bigg/ \left[8\left(1 + M_i / M_j \right) \right]^{\frac{1}{2}}$$

Where:

$\lambda_i^{*,v}$	=	Calculated by the Stiel-Thodos model or the DIPPR thermal conductivity model (Stiel-Thodos/DIPPR)
$\eta_i^{*,v}(p=0)$	=	Obtained from the Chapman-Enskog-Brokaw model
$C_{pi}^{*,ig}$	=	Obtained from the Ideal Gas Heat Capacity model
R	=	Universal gas constant

You must supply parameters for $\eta_i^{*,v}(p=0)$ and $\lambda_i^{*,v}$.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), pp. 530–531.

Diffusivity Models

The Aspen Physical Property System has seven built-in diffusivity models. This section describes the diffusivity models available.

Model	Type
Chapman-Enskog-Wilke-Lee (Binary)	Low pressure vapor
Chapman-Enskog-Wilke-Lee (Mixture)	Low pressure vapor
Dawson-Khoury-Kobayashi (Binary)	Vapor
Dawson-Khoury-Kobayashi (Mixture)	Vapor
Nernst-Hartley	Electrolyte
Wilke-Chang (Binary)	Liquid
Wilke-Chang (Mixture)	Liquid

Chapman-Enskog-Wilke-Lee (Binary)

The binary diffusion coefficient at low pressures $D_{ij}^{v}(p=0)$ is calculated using the Chapman-Enskog-Wilke-Lee model:

$$D_{ij}^{v}(p=0) = \left[2.1989 \times 10^{-22} - 5.0665 \times 10^{-3} f(M) \right] \frac{T^{\frac{2}{3}} f(M)}{\left[p\sigma_{ok}^{2} \Omega_{D} \right]}$$

Where:

$$f(M) = \left[(M_i + M_j)/(M_i M_j) \right]^{\frac{1}{2}}$$

The collision integral for diffusion is:

$$\Omega_D \qquad = \qquad fcn(T, \varepsilon_{ij}/k)$$

The binary size and energy parameters are defined as:

$$\sigma_{ij} \qquad = \qquad \frac{(\sigma_i + \sigma_j)}{2}$$

$$\varepsilon_{ij} \qquad = \qquad (\varepsilon_i \varepsilon_j)^{\frac{1}{2}}$$

Polar parameter δ is used to determine whether to use the Stockmayer or Lennard-Jones potential parameters: ε/k (energy parameter) and σ (collision diameter). To calculate δ, the dipole moment p, and either the Stockmayer parameters or T_b and V_{bm} are needed.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
MW	M_i	—	—	1.0	5000.0	—
MUP	p_i	—	—	0.0	5×10^{-24}	DIPOLEMOMENT
STKPAR/1	$(\varepsilon/k)_{ST}$	$fcn(p_i, T_{bi}, V_{bi})$x	—	—		TEMPERATURE
STKPAR/2	σ_{ST}	$fcn(p_i, T_{bi}, V_{bi})$x	—	—		LENGTH
LJPAR/1	$(\varepsilon/k)_{LJ}$	$fcn(T_{ci}, \omega_i)$ x	—	—		TEMPERATURE
LJPAR/2	σ_{LJ}	$fcn(T_{ci}, p_i, \omega_i)$x	—	—		LENGTH

References

R.C. Reid, J.M. Praunitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 587.

Chapman-Enskog-Wilke-Lee (Mixture)

The diffusion coefficient of a gas into a gas mixture at low pressures is calculated using Blanc's law:

$$D_i^v(p=0) = \sum_{j \neq i} y_j \left[\sum_{j \neq i} \frac{D_{ij}^v(p=0)}{y_j} \right]$$

The binary diffusion coefficient $D_{ij}^v(p=0)$ at low pressures is calculated using the Chapman-Enskog-Wilke-Lee model. (See Chapman-Enskog-Wilke-Lee (Binary).)

You must provide parameters for this model.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
DVBLNC	—	1	x	—	—	—

DVBLNC is set to 1 for a diffusing component and 0 for a non-diffusing component.

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 597.

Dawson-Khoury-Kobayashi (Binary)

The binary diffusion coefficient D_{ij}^v at high pressures is calculated from the Dawson-Khoury-Kobayashi model:

$$D_{ij}^v \rho_m^v = \left[1 + a_1 \rho_{rm}^v + a_2 \left(p_{rm}^v \right)^2 + a_3 \left(p_{rm}^v \right)^3 \right] D_{ig}^v(p=0) \rho_m(p=1atm)$$

$$\rho_{rm}^v = V_{cm}/V_m^v$$

$$\rho_m^v = 1/V_m^v$$

$$V_{cm} = \frac{y_i V_{ci}^* + y_j V_{cj}^*}{y_i + y_j}$$

$D_{ij}^v(p=0)$ is the low-pressure binary diffusion coefficient obtained from the Chapman-Enskog-Wilke-Lee model.

The parameters ρ_m^v and V_m^v are obtained from the Redlich-Kwong equation-of-state model.

You must supply parameters for these two models.

Subscript *i* denotes a diffusing component. *j* denotes a solvent.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
VC	V_{ci}	—	x	0.001	3.5	MOLE-VOLUME

References

R.C. Reid, J.M. Prausnitz, and T.K. Sherwood. *The Properties of Gases and Liquids*, 3rd ed., (New York: McGraw-Hill, 1977), pp. 560-565.

Dawson-Khoury-Kobayashi (Mixture)

The diffusion coefficient of a gas into a gas mixture at high pressure is calculated using Blanc's law:

$$D_i^v = \sum_{j \neq i} y_j \left[\sum_{j \neq i} \frac{D_{ij}^v}{y_j} \right]$$

The binary diffusion coefficient D_{ij}^v at high pressures is calculated from the Dawson-Khoury-Kobayashi model. (See Dawson-Khoury-Kobayashi (Binary).)

You must provide parameters for this model.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
DVBLNC		—	1	—	—	—	—

DVBLNC is set to 1 for a diffusing component and 0 for a nondiffusing component.

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 597.

Nernst-Hartley

The effective diffusivity of an ion i in a liquid mixture with electrolytes can be calculated using the Nernst-Hartley model:

$$D_i = \left(\frac{RT}{z_i F^2}\right)(l_{1,i} + l_{e,i}T)\sum_k x_k \tag{1}$$

Where:

F = 9.65×10^7 C/kmole (Faraday's number)

x_k =   Mole fraction of any molecular species k

z_i =   Charge number of species i

The binary diffusion coefficient of the ion with respect to a molecular species is set equal to the effective diffusivity of the ion in the liquid mixture:

$$D_{ik} \equiv D_i \tag{2}$$

The binary diffusion coefficient of an ion i with respect to an ion j is set to the mean of the effective diffusivities of the two ions:

$$D_{ij} = \frac{(D_i + D_j)}{2}$$

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
CHARGE	z	0.0	—	—	—
IONMOB/1	I_1	—	—	—	AREA, MOLES
IONMOB/2	I_2	0.0	—	—	AREA, MOLES, TEMPERATURE

References

A. L. Horvath, *Handbook of Aqueous Electrolyte Solutions*, (Chichester: Ellis Horwood, Ltd, 1985).

Wilke-Chang (Binary)

The Wilke-Chang model calculates the liquid diffusion coefficient of component i in a mixture at finite concentrations:

$$D_{ij}^l = \left(D_{ij}^{\infty,l}\right)^{x_j} \left(D_{ji}^{\infty,l}\right)^{x_i}$$

The equation for the Wilke-Chang model at infinite dilution is:

$$D_{ij}^{\infty,l} = 1.17282 \times 10^{-16} \frac{(\varphi_j M_j)^{1/2} T}{n_j^l \left(V_{bi}^{*,l}\right)^{0.6}}$$

Where i is the diffusing solute and j the solvent:

φ_j =   Association factor of solvent

n_j^l	=	Liquid viscosity of the solvent calculation. This can be obtained from the Andrade/DIPPR model. You must provide parameters for one of these models.		

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
MW	M_j	—	1.0	5000.0	—
VB	$V_{bi}^{*,l}$	—	0.001	3.5	MOLE-VOLUME

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 598–600.

Wilke-Chang (Mixture)

The Wilke-Chang model calculates the liquid diffusion coefficient of component *i* in a mixture.

The equation for the Wilke-Chang model is:

$$D_i^l = 1.17282 \times 10^{-16} \frac{(\varphi M)^{1/2} T}{n^l (V_{bi}^{*,l})^{0.6}}$$

With:

$$\varphi M = \frac{\sum_{j \neq i} x_j \varphi_j M_j}{\sum_{j \neq i} x_j}$$

Where:

φ_j	=	Association factor of solvent
n^l	=	Mixture liquid viscosity of all nondiffusing components. This can be obtained from the Andrade/DIPPR or another liquid mixture viscosity model. You must provide parameters for one of these models.

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
MW	M_j	—	1.0	5000.0	—
VB	$V_{bi}^{*,l}$	—	0.001	3.5	MOLE-VOLUME
DLWC	—	1	—	—	—

References

R.C. Reid, J.M. Praunsnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987), p. 618.

Surface Tension Models

The Aspen Physical Property System has four built-in surface tension models. This section describes the surface tension models available.

Model	Type
API	Liquid-vapor
IAPS	Water-stream
Hakim-Steinberg-Stiel/DIPPR/IK-CAPE	Liquid-vapor
Onsager-Samaras Electrolyte Correction	Electrolyte liquid-vapor

API Surface Tension

The liquid mixture surface tension for hydrocarbons is calculated using the API model. This model is recommended for petroleum and petrochemical applications. It is used in the CHAO-SEA, GRAYSON, LK-PLOCK, PENG-ROB, and RK-SOAVE option sets. The general form of the model is:

$$\sigma^l = fcn(T, x, T_{bi}, SG, T_{ci})$$

Where:

fcn = A correlation based on API Procedure 10A32 (*API Technical Data Book*, Petroleum Refining, 4th edition)

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
TB	T_{bi}	—	—	4.0	2000.0	TEMPERATURE
SG	SG	—	—	0.1	2.0	—
TC	T_{ci}	—	—	5.0	2000	TEMPERATURE

IAPS Surface Tension for Water

The IAPS surface tension model was developed by the International Association for Properties of Steam. It calculates liquid surface tension for water and steam. This model is used in option sets STEAMNBS and STEAM-TA.

The general form of the equation for the IAPS surface tension model is:

$$\sigma_w = fcn(T, p)$$

Where:

fcn = Correlation developed by IAPS

The model is only applicable to water. No parameters are required.

Hakim-Steinberg-Stiel/DIPPR/IK-CAPE

The liquid mixture surface tension is calculated using the equation:

$$\sigma^l = \sum_i x_i \sigma_i^{*,l}$$

The pure component liquid surface tension can be calculated by three models:

- Hakim-Steinberg-Stiel
- DIPPR liquid surface tension
- IK-CAPE polynomial

Hakim-Steinberg-Stiel

The Hakim-Steinberg-Stiel equation is:

$$\sigma_i^{*,l} = 4.60104 \times 10^{-7} \, p_{ci}^{2/3} T_{ci}^{1/3} Q_{pi} \left(\frac{1 - T_{ri}}{0.4} \right)^{m_i}$$

Where:

$$Q_{pi} = 0.1574 + 0.359\omega_i - 1.769\chi_i - 13.69\chi_i^2 - 0.510\omega_i^2 + 1.298\omega_i\chi_i$$

$$m_i = 1.210 + 0.5385\omega_i - 14.61\chi_i - 32.07\chi_i^2 - 1.656\omega_i^2 + 22.03\omega_i\chi_i$$

The parameter χ_i is the Stiel polar factor.

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
TC	T_{ci}	—	5.0	2000.0	TEMPERATURE
PC	p_{ci}	—	10^5	10^8	PRESSURE
OMEGA	ω_i	—	-0.5	2.0	—
CHI	χ_i	0	—	—	—

DIPPR Liquid Surface Tension

The DIPPR equation for liquid surface tension is:

$$\sigma_i^{*,l} = C_{1i}\left(1 - T_{ri}\right)^{\left(C_{2i} + C_{3i}T_{ri} + C_{4i}T_{ri}^2 + C_{5i}T_{ri}^3\right)} \quad \text{for} \quad C_{6i} \leq T \leq C_{7i}$$

Where:

$$T_{ri} \quad = \quad T/T_{ci}$$

If the SIGDIP parameters for a given component are available, the Aspen Physical Property System uses the DIPPR equation. The DIPPR model is also used by PCES.

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
SIGDIP/1	C_{1i}	—	—	—	SURFACE-TENSION
SIGDIP/2, . . . , 5	$C_{2i},...,C_{5i}$	0	—	—	—
SIGDIP/6	C_{6i}	0	—	—	TEMPERATURE
SIGDIP/7	C_{7i}	1000	—	—	TEMPERATURE

IK-CAPE Polynomial

The IK-CAPE model is a polynomial equation containing 10 terms. If the parameter SIGPO is available, the Aspen Physical Property System uses the IK-CAPE equation.

$$\sigma_i^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

for $C_{11i} \leq T \leq C_{12i}$

Linear extrapolation of $\sigma_i^{*,l}$ versus T occurs outside of bounds.

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
SIGPO/1	C_{1i}	—	x	—	—	SURFACE-TENSION
SIGPO/2, ... , 10	$C_{2i},...,C_{10i}$	0	x	—	—	SURFACE-TENSION TEMPERATURE
SIGPO/11	C_{11i}	0	x	—	—	TEMPERATURE
SIGPO/12	C_{12i}	1000	x	—	—	TEMPERATURE

References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th. ed., (New York: McGraw-Hill, 1987), p. 638.

Onsager-Samaras

The Onsager-Samaras model calculates the correction to the liquid mixture surface tension ofa solvent mixture, due to the presence of electrolytes:

$$\sigma = \sigma_{solv} + \sum_{ca} x_{ca}^a \Delta\sigma_{ca} \qquad (1)$$

Where:

σ_{solv}	=	Surface tension of the solvent mixture calculated by the Hakim-Steinberg-Stiel model
x_{ca}^a	=	Mole fraction of the apparent electrolyte *ca*
$\Delta\sigma_{ca}$	=	Contribution to the surface tension correction due to apparent electrolyte *ca*

For each apparent electrolyte ca, the contribution to the surface tension correction is calculated as:

$$\Delta\sigma_{ca} = \frac{80.0}{\varepsilon_{solv}} c_{ca}^a \log\left\{\frac{1.13\text{x}10^{-13}(\varepsilon_{solv}T)^3}{c_{ca}^a}\right\}$$ (2)

Where:

ε_{solv}	$=$	Dielectric constant of the solvent mixture
c_{ca}^a	$=$	$\dfrac{x_{ca}^a}{V_m^l}$
V_m^l	$=$	Liquid molar volume calculated by the Clarke model

Apparent electrolyte mole fractions are computed from the true ion mole-fractions and ionic charge number. They are also computed if you use the apparent component approach. See Chapter 5 for a more detailed discussion of this method.

You must provide parameters for the Hakim-Steinberg-Stiel model, used for the calculation of the surface tension of the solvent mixture.

Parameter Name/Element	Symbol	Default	Lower Limit	Upper Limit	Units
CHARGE	z	0.0	—	—	—

References

A. L. Horvath, *Handbook of Aqueous Electrolyte Solutions*, (Chichester: Ellis, Ltd. 1985).

Nonconventional Solid Property Models

This section describes the nonconventional solid density and enthalpy models available in the Aspen Physical Property System. The following table lists the available models and their model names. Nonconventional components are solid components that cannot be characterized by a molecular formula. These components are treated as pure components, though they are complex mixtures.

Nonconventional Solid Property Models

General Enthalpy and Density Models	Model name	Phase(s)
General density polynomial	DNSTYGEN	S
General heat capacity polynomial	ENTHGEN	S

Enthalpy and Density Models for Coal and Char	Model name	Phase(s)
General coal enthalpy model	HCOALGEN	S
IGT coal density model	DCOALIGT	S
IGT char density model	DCHARIGT	S

General Enthalpy and Density Models

The Aspen Physical Property System has two built-in general enthalpy and density models. This section describes the general enthalpy and density models available.

Model

General Density Polynomial

General Heat Capacity Polynomial

General Density Polynomial

DNSTYGEN is a general model that gives the density of any nonconventional solid component. It uses a simple mass fraction weighted average for the reciprocal temperature-dependent specific densities of its individual constituents. There may be up to twenty constituents with mass percentages. You must define these constituents, using the general component attribute GENANAL. The equations are:

$$\rho_i^s = \frac{1}{\sum_i \dfrac{w_{ij}}{\rho_{ij}}}$$

$$\rho_{i,j}^s = a_{i,j1} + a_{i,j2}T + a_{i,j3}T^2 + a_{i,j4}T^3$$

Where:

w_{ij}	=	Mass fraction of the *j*th constituent in component *i*
$\rho_{i,j}^s$	=	Density of the *j*th consituent in component *i*

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit
DENGEN/1+4 (J-1)	$a_{i,j1}$	x	—	—	—
DENGEN/2+4 (J-1)	$a_{i,j2}$	x	0	—	—
DENGEN/3+4 (J-1)	$a_{i,j3}$	x	0	—	—
DENGEN/4+4 (J-1)	$a_{i,j4}$	x	0	—	—

The units are MASS-DENSITY and TEMPERATURE.

Use the elements of GENANAL to input the mass percentages of the constituents. The structure of DENGEN is: four coefficients for the first constituent, four coefficients for the second constituent, and so on.

General Heat Capacity Polynomial

ENTHGEN is a general model that gives the specific enthalpy of any nonconventional component as a simple mass-fraction-weighted-average for the enthalpies of its individual constituents. You may define up to twenty constituents with mass percentages, using the general component attribute GENANAL. The specific enthalpy of each constituent at any temperature is calculated by combining specific enthalpy of formation of the solid with a sensible heat change. (See Chapter 1.)

The equations are:

$$h_i^s = \sum_i w_{i,j} h_{i,j}^s$$

$$h_{i,j}^s = \Delta_f h_j^s + \int_{298.15}^{T} C_{p,j}^s dT$$

$$C_{p,j}^s = a_{i,j1} + a_{i,j2}T + a_{i,j3}T^2 + a_{i,j4}T^3$$

Where:

w_{ij}	=	Mass fraction of the jth constituent in component *i*
h_i^s	=	Specific enthalpy of solid component *i*
$\Delta_f h_j^s$	=	Specific enthalpy of formation of constituent *j*
$C_{P_{i,j}}^s$	=	Heat capacity of the *j*th constituent in component *i*

Parameter Name/Element	Symbol	Default	MDS	Lower Limit	Upper Limit	Units
DHFGEN/J	$\Delta_f h_j^s$	x	0	—	—	MASS-ENTHALPY
HCGEN/1+4 (J-1)	$a_{i,j1}$	x	—	—	—	See note.
HCGEN/2+4	$a_{i,j2}$	x	0	—	—	See note.
HCGEN/3+4 (J-1)	$a_{i,j3}$	x	0	—	—	See note.
HCGEN/4+4 (J-1)	$a_{i,j4}$	x	0	—	—	See note.

The units for HCGEN are MASS-ENTHALPY and TEMPERATURE.

The elements of GENANAL are used to input the mass percentages of the constituents. The structure for HCGEN is: four coefficients for the first constituent, four coefficients for the second constituent, and so on.

Enthalpy and Density Models for Coal and Char

Coal is modeled in the Aspen Physical Property System as a nonconventional solid. Coal models are empirical correlations, which require solid material characterization information. Component attributes are derived from constituent analyses. Definitions of coal component attributes are given in the Aspen Plus User Guide, Chapter 6.

Enthalpy and density are the only properties calculated for nonconventional solids. This section describes the special models available in the Aspen Physical Property System for the enthalpy and density of coal and char. The component attributes required by each model are included. The coal models are:

- General coal enthalpy
- IGT Coal Density
- IGT Char Density

Notation

Most correlations for the calculation of coal properties require proximate, ultimate, and other analyses. These are converted to a dry, mineral-matter-free basis. Only the organic portion of the coal is considered.

Moisture corrections are made for all analyses except hydrogen, according to the formula:

$$w^d = \left(\frac{w}{1 - w_{H_2O}} \right)$$

Where:

w = The value determined for weight fraction

$$w^d \quad = \quad \text{The value on a dry basis}$$

$$w_{H_2O} \quad = \quad \text{The moisture weight fraction}$$

For hydrogen, the formula includes a correction for free-moisture hydrogen:

$$w_H^d = \frac{w_H - 0.119 w_{H_2O}}{1 - w_{H_2O}}$$

The mineral matter content is calculated using the modified Parr formula:

$$w_{MM} = 1.13 w_A + 0.47 w_{Sp} + w_{Cl}$$

The ash term corrects for water lost by decomposition of clays in the ash determination. The average water constitution of clays is assumed to be 11.2 percent. The sulfur term allows for loss in weight of pyritic sulfur when pyrite is burned to ferric oxide. The original Parr formula assumed that all sulfur is pyritic sulfur. This formula included sulfatic and organic sulfur in the mineral-matter calculation. When information regarding the forms of sulfur is available, use the modified Parr formula to give a better approximation of the percent of inorganic material present. Because chlorine is usually small for United States coals, you can omit chlorine from the calculation.

Correct analyses from a dry basis to a dry, mineral-matter-free basis, using the formula:

$$w^{dm} = \frac{w^d - \Delta w^d}{1 - w_{MM}}$$

Where:

$$\Delta w^d \quad = \quad \text{Correction factor for other losses, such as the loss of carbon in carbonates and the loss of hydrogen present in the water constitution of clays}$$

$$\Delta w_C^d = 0.014 W_A^d + 0.005 W_{sp}^d$$

$$\Delta w_H^d = 0.013 w_A^d - 0.02 w_{Sp}^d$$

The oxygen and organic sulfur contents are usually calculated by difference as:

$$W_O^{dm} = 1 - W_C^{dm} - W_H^{dm} - W_{So}^{dm} - W_N^{dm}$$

$$w_S^{dm} = w_{St}^{dm} - w_{Sp}^{dm} - w_{Ss}^{dm}$$

Where:

C_p	=	Heat capacity / (J/kgK)
c_p	=	Heat capacity / (cal/gC)
h	=	Specific enthalpy
$\Delta_c h$	=	Specific heat of combustion
$\Delta_f h$	=	Specific heat of formation
R_O	=	Mean-maximum relectance in oil
T	=	Temperature/K
t	=	Temperature/C
w	=	Weight fraction
ρ	=	Specific density

Subscripts:

A	=	Ash
C	=	Carbon
Cl	=	Chlorine
FC	=	Fixed carbon
H	=	Hydrogen
H_2O	=	Moisture
MM	=	Mineral matter
N	=	Nitrogen
O	=	Oxygen
So	=	Organic sulfur
Sp	=	Pyritic sulfur
St	=	Total sulfur
S	=	Other sulfur
VM	=	Volatile matter

Superscripts:

d	=	Dry basis
m	=	Mineral-matter-free basis

General Coal Enthalpy Model

The general coal model for computing enthalpy in the Aspen Physical Property System is HCOALGEN. This model includes a number of different correlations for the following:

- Heat of combustion
- Heat of formation
- Heat capacity

You can select one of these correlations using an option code in the Properties Advanced NC-Props form. (See the Aspen Plus User Guide, Chapter 6). Use option codes to specify a calculation method for properties. Each element in the option code vector is used in the calculation of a different property.

The table labeled HCOALGEN Option Codes (below) lists model option codes for HCOALGEN. The table is followed by a detailed description of the calculations used for each correlation.

The correlations are described in the following section. The component attributes are defined in Aspen Plus User Guide, Chapter 6.

Heat of Combustion Correlations

The heat of combustion of coal in the HCOALGEN model is a gross calorific value. It is expressed in Btu/lb of coal on a dry mineral-matter-free basis. ASTM Standard D-2015 defines standard conditions for measuring gross calorific value. Initial oxygen pressure is 20 to 40 atmospheres. Products are in the form of ash; liquid water; and gaseous CO_2, SO_2, and NO_2.

You can calculate net calorific value from gross calorific value by making a deduction for the latent heat of vaporization of water.

Heat of combustion values are converted back to a dry, mineral-matter-containing basis with a correction for the heat of combustion of pyrite. The formula is:

$$\Delta_c h_i^d = (1 - w_{MMi})\Delta_c h_i^{dm} + 5400 w_{sp,i}$$

The heat of combustion correlations were evaluated by the Institute of Gas Technology (IGT). They used data for 121 samples of coal from the Penn State Data Base (IGT, 1976) and 457 samples from a USGS report (Swanson, et al., 1976). These samples included a wide range of United States coal fields. The constant terms in the HCOALGEN correlations are bias corrections obtained from the IGT study.

Boie Correlation:

$$\Delta_c h_i^{dm} = \left[a_{1i} w_{C,i}^{dm} + a_{2i} w_{H,i}^{dm} + a_{3i} w_{St,i}^{dm} + a_{4i} w_{O,i}^{dm} + a_{5i} w_{N,i}^{dm} \right] 10^2 + a_{6i}$$

Parameter Name/Element	Symbol	Default
BOIEC/1	a_{1i}	151.2
BOIEC/2	a_{2i}	499.77
BOIEC/3	a_{3i}	45.0
BOIEC/4	a_{4i}	-47.7
BOIEC/5	a_{5i}	27.0
BOIEC/6	a_{6i}	-189.0

Dulong Correlation:

$$\Delta_c h_i^{dm} = \left[a_{1i} w_{C,i}^{dm} + a_{2i} w_{H,i}^{dm} + a_{3i} w_{S,i}^{dm} + a_{4i} w_{O,i}^{dm} + a_{5i} w_{N,i}^{dm} \right] 10^2 + a_{5i}$$

Parameter Name/Element	Symbol	Default
DLNGC/1	a_{1i}	145.44
DLNGC/2	a_{2i}	620.28
DLNGC/3	a_{3i}	40.5
DLNGC/4	a_{4i}	-77.54
DLNGC/5	a_{5i}	-16.0

Grummel and Davis Correlation:

$$\Delta_c h_i^{dm} = \frac{\left(a_{5i} + a_{2i} w_{H,i}^{dm} \right)}{\left(1 - w_{A,i}^d \right)} \left(a_{1i} w_{C,i}^{dm} + a_{2i} w_{H,i}^{dm} + a_{3i} w_{S,i}^{dm} + a_{4i} w_{O,i}^{dm} \right) 10^2 + a_{6i}$$

Parameter Name/Element	Symbol	Default
GMLDC/1	a_{1i}	0.3333
GMLDC/2	a_{2i}	654.3
GMLDC/3	a_{3i}	0.125
GMLDC/4	a_{4i}	0.125
GMLDC/5	a_{5i}	424.62
GMLDC/6	a_{6i}	-2.0

Mott and Spooner Correlation:

$$\Delta_c h_i^{dm} = \left[a_{1i} w_{C,i}^{dm} + a_{2i} w_{H,i}^{dm} + a_{3i} w_{S,i}^{dm} - a_{4i} w_{O,i}^{dm} \right] 10^2 + a_{7i} \quad \text{for} \quad w_{O,i}^{dm} \le 0.15$$

$$\Delta_c h_i^{dm} = \left[a_{1i} w_{C,i}^{dm} + a_{2i} w_{H,i}^{dm} + a_{3i} w_{S,i}^{dm} - \left(a_{6i-} \frac{a_{5i} w_{O,i}^{dm}}{1 - w_{A,i}^d} \right) w_{O,i}^{dm} \right] 10^2 + a_{7i} \quad \text{for} \quad w_{O,i}^{dm} \le 0.15$$

Parameter Name/Element	Symbol	Default
MTSPC/1	a_{1i}	144.54
MTSPC/2	a_{2i}	610.2
MTSPC/3	a_{3i}	40.3
MTSPC/4	a_{4i}	62.45
MTSPC/5	a_{5i}	30.96
MTSPC/6	a_{6i}	65.88
MTSPC/7	a_{7i}	-47.0

IGT Correlation:

$$\Delta_c h_i^{dm} = \left[a_{1i} w_{C,i}^d + a_{2i} w_{H,i}^d + a_{3i} w_{S,i}^d + a_{4i} w_{A,i}^d \right] 10^2 + a_{5i}$$

Parameter Name/Element	Symbol	Default
CIGTC/1	a_{1i}	178.11
CIGTC/2	a_{2i}	620.31
CIGTC/3	a_{3i}	80.93
CIGTC/4	a_{4i}	44.95
CIGTC/5	a_{5i}	-5153.0

User Input Value of Heat Combustion

Parameter Name/Element	Symbol	Default
HCOMB	$\Delta_c h_i^d$	0

Standard Heat of Formation Correlations

There are two standard heat of formation correlations for the HCOALGEN model:

- Heat of combustion-based
- Direct

Heat of Combustion-Based Correlation This is based on the assumption that combustion results in complete oxidation of all elements except sulfatic sulfur and ash, which are considered inert. The numerical coefficients are combinations of stoichiometric coefficients and heat of formation for CO_2, H_2O, HCl, and NO_2 .at 298.15K:

$$\Delta_f h_i^d = \Delta_c h_i^d - (1.418 \times 10^6 w_{H,i}^d + 3.278 \times 10^5 w_{C,i}^d + 9.264 \times 10^4 w_{S,i}^d$$
$$- 2.418 \times 10^6 w_{N,i}^d - 1.426 \times 10^4 w_{Cl,i}^d)10^2$$

Direct Correlation Normally small, relative to its heat of combustion. An error of 1% in the heat of a combustion-based correlation produces about a 50% error when it is used to calculate the heat of formation. For this reason, the following direct correlation was developed, using data from the Penn State Data Base. It has a standard deviation of 112.5 Btu/lb, which is close to the limit, due to measurement in the heat of combustion:

$$\Delta_f h_i^d = \left[a_{1i} w_{c,i}^{dm} + a_{2i} w_{H,i}^{dm} + a_{3i} w_{H,i}^d + a_{4i} w_{Sp}^d + a_{5i} w_{Ss}^d \right]10^2$$
$$+ a_{6i} R_{o,i} + \left[a_{7i} \left(w_{C,i}^d + w_{FC,i}^d \right) + a_{8i} w_{VM}^d \right]10^2$$
$$+ \left[a_{9i} \left(w_{C,i}^{dm} \right)^2 + a_{10i} \left(w_{St,i}^{dm} \right)^2 + a_{11i} \left(w_{c,i}^d - w_{FC,i}^d \right)^2 + a_{12i} \left(w_{VM,i}^d \right)^2 \right]10^4$$
$$+ a_{13i} \left(R_{o,i} \right)^2 + a_{14i} \left(w_{VM,i}^d \right)\left(w_{C,i}^d - w_{FC,i}^d \right)10^4 + a_{15i}$$

Where:

Parameter Name/Element	Symbol	Default
HFC/1	a_{1i}	1810.123
HFC/2	a_{2i}	-502.222
HFC/3	a_{3i}	329.1087
HFC/4	a_{4i}	121.766
HFC/5	a_{5i}	-542.393
HFC/6	a_{6i}	1601.573
HFC/7	a_{7i}	424.25
HFC/8	a_{8i}	-525.199
HFC/9	a_{9i}	-11.4805
HFC/10	a_{10i}	31.585
HFC/11	a_{11i}	13.5256
HFC/12	a_{12i}	11.5
HFC/13	a_{13i}	-685.846
HFC/14	a_{14i}	-22.494
HFC/15	a_{15i}	-64836.19

Heat Capacity Kirov Correlations

The Kirov correlation (1965) considered coal to be a mixture of moisture, ash, fixed carbon, and primary and secondary volatile matter. Primary volatile matter is any volatile matter equal to the

total volatile matter content, up to 10%. The correlation developed by Kirov treats the heat capacity as a weighted sum of the heat capacities of the constituents:

$$C_{p,i}^d = \sum_{j=1}^{ncn} w_j C_{p,ij}$$

$$C_{p,ij} = a_{i,j1} + a_{i,j2}T + a_{i,j3}T^2 + a_{i,j4}T^3$$

Where:

i	=	Component index
j	=	Constituent index $j = 1, 2, \ldots, ncn$
1	=	Moisture
2	=	Fixed carbon
3	=	Primary volatile matter
4	=	Secondary volatile matter
5	=	Ash
w_j	=	Mass fraction of jth constituent on dry basis

Parameter Name/Element	Symbol	Default
CP1C/1	$a_{i,11}$	1.0
CP1C/2	$a_{i,12}$	0
CP1C/3	$a_{i,13}$	0
CP1C/4	$a_{i,14}$	0
CP1C/5	$a_{i,21}$	0.165
CP1C/6	$a_{i,22}$	6.8×10^{-4}
CP1C/7	$a_{i,23}$	-4.2×10^{-7}
CP1C/8	$a_{i,24}$	0
CP1C/9	$a_{i,31}$	0.395
CP1C/10	$a_{i,32}$	8.1×10^{-4}
CP1C/11	$a_{i,33}$	0
CP1C/12	$a_{i,34}$	0
CP1C/13	$a_{i,41}$	0.71
CP1C/14	$a_{i,42}$	6.1×10^{-4}
CP1C/15	$a_{i,43}$	0

CP1C/16	$a_{i,44}$	0
CP1C/17	$a_{i,51}$	0.18
CP1C/18	$a_{i,52}$	1.4×10^{-4}
CP1C/19	$a_{i,53}$	0
CP1C/20	$a_{i,54}$	0

Cubic Temperature Equation

The cubic temperature equation is:

$$c_p^d = a_{1i} + a_{2i}t + a_{3i}t^2 + a_{4i}t^3$$

Parameter Name/Element	Symbol	Default
CP2C/1	a_{1i}	0.438
CP2C/2	a_{2i}	-7.576×10^{-3}
CP2C/3	a_{3i}	8.793×10^{-5}
CP2C/4	a_{4i}	-2.587×10^{-7}

The default values of the parameters were developed by Gomez, Gayle, and Taylor (1965). They used selected data from three lignites and a subbituminous B coal, over a temperature range from 32.7 to 176.8°C.

HCOALGEN Option Codes

Option Code Number	Option Code Value	Calculation Method	Parameter Names	Component Attributes
1 Heat of Combustion				
	1	Boie correlation	BOIEC	ULTANAL SULFANAL PROXANAL
	2	Dulong correlation	DLNGC	ULTANAL SULFANAL PROXANAL
	3	Grummel and Davis correlation	GMLDC	ULTANAL SULFANAL PROXANAL
	4	Mott and Spooner correlation	MTSPC	ULTANAL SULFANAL PROXANAL
	5	IGT correlation	CIGTC	ULTANAL PROXANAL
	6	User input value	HCOMB	ULTANAL PROXANAL

Option Code Number	Option Code Value	Calculation Method	Parameter Names	Component Attributes
2 Standard Heat of Formation				
	1	Heat-of-combusion- based correlation	—	ULTANAL SULFANAL
	2	Direct correlation	HFC	ULTANAL SULFANAL PROXANAL
3 Heat Capacity				
	1	Kirov correlation	CP1C	PROXANAL
	2	Cubic temperature equation	CP2C	—
4 Enthalpy Basis				
	1	Elements in their standard states at 298.15K and 1 atm	— —	— —
	2	Component at 298.15 K	—	—

Default = 1 for each option code

IGT (Institute of Gas Technology), *Coal Conversion Systems Technical Data Book*, Section PMa. 44.1, 1976.

V.E. Swanson et al., *Collection, Chemical Analysis and Evaluation of Coal Samples in 1975*, U.S. Geological Survey, Open-File Report (1976), pp. 76–468.

N.Y. Kirov, "Specific Heats and Total Heat Contents of Coals and Related Materials are Elevated Temperatures," *BCURA Monthly Bulletin*, (1965), pp. 29, 33.

M. Gomez, J.B. Gayle, and A.R. Taylor, Jr., *Heat Content and Specific Heat of Coals and Related Products*, U.S. Bureau of Mines, R.I. 6607, 1965.

IGT Coal Density Model   The DCOALIGT model gives the true (skeletal or solid-phase) density of coal on a dry basis. It uses ultimate and sulfur analyses. The model is based on equations from IGT (1976):

$$\rho_i = \frac{\rho_i^{dm}}{\left[\rho_i^{dm}\left(0.42 w_{A,i}^d - 0.15 w_{Sp,i}^d \right) + 1 - 1.13 w_{A,i}^d - 0.5475 w_{Sp,i}^d \right]}$$

$$\rho_i^{dm} = \frac{1}{a_{1i} + a_{2i} w_{H,i}^{dm} + a_{3i}\left(w W_{H,i}^{d,m} \right) + a_{4i}\left(w_{H,i}^{dm} \right)^3}$$

$$W_{H,i}^{dm} = \frac{10^2 \left(W_{H,i}^d - 0.013 w_{A,i}^d + 0.02 w_{Sp,i}^d \right)}{\left(1 - 1.13 w_{A,i}^d - 0.475 w_{Sp,i}^d \right)}$$

The equation for ρ_i^{dm} is good for a wide range of hydrogen contents, including anthracites and high temperature cokes. The standard deviation of this correlation for a set of 190 points collected by IGT from the literature was $12 \times 10^{-6} \text{ m}^3/\text{kg}$. The points are essentially uniform over the whole range. This is equivalent to a standard deviation of about 1.6% for a coal having a hydrogen content of 5%. It increases to about 2.2% for a coke or anthracite having a hydrogen content of 1%.

Parameter Name/Element	Symbol	Default
DENIGT/1	a_{1i}	0.4397
DENIGT/2	a_{2i}	0.1223
DENIGT/3	a_{3i}	-0.01715
DENIGT/4	a_{4i}	0.001077

IGT Char Density Model   The DGHARIGT model gives the true (skeletal or solid-phase) density of char or coke on a dry basis. It uses ultimate and sulfur analyses. This model is based on equations from IGT (1976):

$$\rho_i^d = \frac{3\rho_i^{dm}}{w_{A,i}^d \rho_i^{dm} + 3\left(1 - w_{A,i}^d \right)}$$

$$\rho_i^d = \frac{1}{a_{1i} + a_{2i} w_{H,i}^{dm} + a_{2i} \left(w_{H,i}^{d,m} \right)^2 + a_{3i} \left(w_{H,i}^{dm} \right)^3}$$

$$w_{H,i}^{dm} = \frac{w_{H,i}^d}{\left(1 - w_{A,i}^d \right)}$$

Parameter Name/Element	Symbol	Default
DENIGT/1	a_{1i}	0.4397
DENIGT/2	a_{2i}	0.1223
DENIGT/3	a_{3i}	-0.01715
DENIGT/4	a_{4i}	0.001077

The densities of graphitic high-temperature carbons (including cokes) range from 2.2×10^3 to $2.26 \times 10^3 \text{ kg}/\text{m}^3$. Densities of nongraphitic high-temperature carbons (derived from chars) range from 2.0×10^3 to $2.2 \times 10^3 \text{ kg}/\text{m}^3$. Most of the data used in developing this correlation were for carbonized coking coals.

Although data on a few chars (carbonized non-coking coals) were included, none has a hydrogen content less than 2%. The correlation is probably not accurate for high temperature chars.

References

I.M. Chang, B.S. Thesis, Massachusetts Institute of Technology, 1979.

M. Gomez, J.B. Gayle, and A.R. Taylor, Jr., *Heat Content and Specific Heat of Coals and Related Products*, U.S. Bureau of Mines, R.I. 6607, 1965.

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Property Calculation Methods and Routes

Overview

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*.

The Aspen Plus User Guide, Chapter 7, 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:

$$\varphi_i^l = \gamma_i \varphi_i^{*,l} \tag{1}$$

Where:

$$\varphi_i^{*,l} = \varphi_i^{*,v} \frac{p_i^{*,l}}{p} \tag{2}$$

Equations 1 and 2 are both derived from thermodynamics. The equations relate the properties of interest $\left(\varphi_i^l, \varphi_i^{*,l}\right)$ to other properties $\left(\gamma_i, \varphi_i^{*,v}, p_i^{*,l}\right)$ 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 $\left(p_i^{*,l}\right)$

- 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, this chapter.

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 Chapter 2. Routes are discussed in detail in Routes and Models, this chapter.

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, this chapter).

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, this chapter.

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 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
PHIV	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_i^{v}	Vapor mixture molar enthalpy
HLMX	H_i^{l}	Liquid mixture molar enthalpy
HSMX	H_i^{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

Property Name	Symbol	Description
GS	$\mu_i^{*,s}$	Solid pure component molar Gibbs free energy
GVMX	G_i^v	Vapor mixture molar Gibbs free energy
GLMX	G_i^l	Liquid mixture molar Gibbs free energy
GSMX	G_i^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_i^v	Vapor mixture molar entropy
SLMX	S_i^l	Liquid mixture molar entropy
SSMX	S_i^s	Solid mixture molar entropy
VV	$V_i^{*,v}$	Vapor pure component molar volume
VL	$V_i^{*,l}$	Liquid pure component molar volume
VS	$V_i^{*,s}$	Solid pure component molar volume
VVMX	V_i^v	Vapor mixture molar volume
VLMX	V_i^l	Liquid mixture molar volume
VSMX	V_i^s	Solid mixture molar volume
MUV	$\eta_i^{*,v}$	Vapor pure component viscosity
MUL	$\eta_i^{*,l}$	Liquid pure component viscosity
MUVMX	η_i^v	Vapor mixture viscosity
MULMX	η_i^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_i^v	Vapor mixture thermal conductivity

Property Name	Symbol	Description
KLMX	λ_i^l	Liquid mixture thermal conductivity
KSMX	λ_i^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
SIGL	$\sigma_i^{*,l}$	Pure component surface tension
SIGLMX	σ^l	Mixture surface tension

Property Name	Symbol	Description
DHV	$H_i^{*,v} - H_i^{*,ig}$	Vapor pure component molar enthalpy departure
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	$H_i^{*,l}(p) - H_i^{*,l}(p_i^*)$	Liquid pure component molar enthalpy departure pressure correction
DHSPC	$H_i^{*,s}(p) - H_i^{*,s}(p_i^*)$	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

Property Name	Symbol	Description
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
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

Property Name	Symbol	Description
HNRYPC	θ_{iA}^{∞}	Henry's constant pressure correction for supercritical component i in subcritical component A
XTRUE	x_{true}	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	$\lambda_i^{*,v}(p=0) - \lambda_i^{*,v}(p$	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:

$$H_i^{*,l} - H_i^{*,ig} = H_i^{*,v} - H_i^{*,ig} - \Delta_{vap} H_i$$

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:

$$H_i^{*,l} - H_i^{*,ig} = f(p,T,\text{correlation parameters})$$

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:

$$H_i^{*,l} - H_i^{*,ig} = f(p,T,\text{specified model})$$

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:, which appear later in this chapter:

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 Chapter 1). 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, this chapter).

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.

$$H^l = f^l(T, p, x_i, parameters)$$

Method 2 HLMX is calculated from the ideal liquid mixture enthalpy and excess enthalpy.

$$H_m^l = \sum x_i H_i^{*,l} + H_m^{E,l}$$

$$\left(HLMX = \sum x_i HL_i + HLXS\right)$$

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.

$$H_m^l = H_m^{ig} + \left(H_m^l - H_m^{ig}\right)$$

$$\left(HLMX = HIGMX + DHLMX\right)$$

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

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\varphi_i^{*,v}$ PHIV	Major	1	Specified model	$\varphi_i^{*,v}$ Model name
φ_i^{v} PHIVMX	Major	1	Specified model	φ_i^{v} Model name (Default: $\varphi_i^{v} = 1$)
		2	$\varphi_i^{v} = f\left(y_i, \varphi_i^{*,v}\right)$	$\varphi_i^{*,v}$ Route ID φ_i^{v} Model name
		3	$\varphi_i^{v} = f\left(\gamma_i\right)$	γ_i Model name φ_i^{v} Model name

Liquid Fugacity
Coefficient Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\varphi_i^{*,l}$ PHIL	Major	1	Specified model	$\varphi_i^{*,l}$ Model name
		2	$$\dfrac{\varphi_i^{*,v}\left(T, p_i^{*,l}\right) p_i^{*,l} \theta_i^{*,l}}{p}$$	$p^{*,l}$ Model name $\varphi_i^{*,v}$ Model name (Default: $\varphi^{*,v}=1$) $\theta^{*,l}$ Route ID (Default: $\theta_i^{*,l}=1$
		3	Specified model for supercritical 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
$\theta_i^{*,l}$ PHILPC	Subord.	1	$$\exp\left(\frac{1}{RT}\int_{p_i^{*,l}}^{p} V^{*,l}dp\right)$$	$p^{*,l}$ Model name $V_i^{*,l}$ Model Name Integration option code (Default:1 point)
		2	Specified model	$\theta_i^{*,l}$ Model name
φ_i^{l} PHILMX	Major	1	Specified model	φ_i^{l} Model name
		2	$\gamma_i\varphi_i^{*,l}\theta_i^{E}$	γ_i Model name (Default: $\gamma_i=1$) $\varphi_i^{*,l}$ Route ID θ_i^{E} Route ID (Default: $\theta_i^{E}=1$)
		3	Unsymmetric Convention For subcritical components (A or B): $$\varphi_A^{l}=\delta_A\gamma_A\varphi_A^{*,l}$$	$\varphi_A^{*,l}$ Route ID γ_A Model name (Default: $\gamma_A=1$)

For supercritical components (i or j)

$$\varphi_i^l = \gamma_i \left(\frac{H_i}{p\gamma_i^\infty} \right)$$

Where:

$$\ln \delta_A = \frac{w_A}{x_A} \sum_j x_j \left[\ln\left(\frac{H_{iA}}{\gamma_{jA}^\infty} \right) - \ln\left(\frac{H_j}{\gamma_j^\infty} \right) \right] \quad H_{jA} \text{ Route ID}$$

$$\ln\left(\frac{H_i}{\gamma_i^\infty} \right) = \sum_B w_B \ln\left(\frac{H_{iB}}{\gamma_{iB}^\infty} \right) \qquad\qquad w_B \text{ Model name}$$

$$\ln \gamma_i^\infty = \lim_{\sum_j x_j \to 0} (\ln \gamma_i) \qquad\qquad w_B \text{ Model option code (see Model Option Code Help)}$$

$$\sum_B w_B = 1 \qquad\qquad\qquad\qquad \text{Method Option code}$$

0: Do not calculate H_i

1: Calculate H_i
(Default = 0)

| | | 4 | $\gamma_i \varphi_i^{*,l} \theta_i^E$ | γ_i Model name |

(Default: $\gamma_i = 1$)

$\varphi_i^{*,l}$ Route ID

θ_i^E Route ID

(Default: $\theta_i^E = 1$)

Where:

$$\gamma_i = f(x^t)$$

(Default: $\theta_i^E = 1$)

x^t Route ID

| | | 5 | Unsymmetric Convention | |

For subcritical components (A or B): $\varphi_i^{*,l}$ Route ID

$$\varphi_A^l = \delta_A \gamma_A \varphi_A^{*,l}$$

γ_A Model name

(Default: $\gamma_A = 1$)

Where:

$$\gamma_A = f(x^t)$$

x^t Route ID

For supercritical components (i or j)

$$\varphi_i^l = \gamma_i \left(\frac{H_i}{p\gamma_i^\infty} \right)$$

Property Symbol and Name	Type	Method Code	Method	Route Structure Information Required
			Where:	
			$$\ln \delta_A = \frac{W_A}{X_A} \sum_j x_j \left[\ln\left(\frac{H_{iA}}{\gamma_{jA}^\infty}\right) - \ln\left(\frac{H_j}{\gamma_j^\infty}\right)\right]$$	H_{jA} Route ID
			$$\ln\left(\frac{H_i}{\gamma_i^\infty}\right) = \sum_B w_B \ln\left(\frac{H_{iB}}{\gamma_{iB}^\infty}\right)$$	w_B Model name
			$$\ln\gamma_i^\infty = \lim_{\sum_j x_j \to 0}(\ln\gamma_i)$$	w_B Model option code (see Model Option Code Help)
			$$\sum_B w_B = 1$$	Method Option code
				0: Do not calculate H_i
				1: Calculate H_i
				(Default = 0)
		6	$\varphi_i^l = f(\gamma_i)$	γ_i Model name
				φ_i^l Model name
x^t XTRUE	Subord.	1	$x^t = f(T, x_i, \gamma_i, \text{Chemistry})$	γ_i Model name
θ_i^E GAMPC	Subord.	1	$\exp\left(\frac{1}{RT}\int_{p^{ref}}^{p}\left(V_i^l - V_i^{*,l}\right)dp\right)$	V_i^l Model name
				$V_i^{*,l}$ Model name
				Integration option code (Default: 1 point)
		2	Specified model	θ_i^E Model name
$\theta_i^{*,E}$ GAMPC1	Subord.	1	$\exp\left(\frac{1}{RT}\int_{p^{ref}}^{p}V_i^l\,dp\right)$	V_i^l Model name
				Integration option code (Default: 1 point)
		2	Specified model	$\theta_i^{*,E}$ Model name
H_{iA} HNRY	Subord.	1	Specified model	H_{iA} Model name
		2	$H_{iA}\left(p^{ref}, T\right)\theta_{iA}^\infty$	H_{iA} Model name
				θ_{iA}^∞ Route ID
				(Default: $\theta_{iA}^\infty = 1$)

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required

θ_{iA}^{∞}
HNRYPC
	Subord.	1	$\exp\left(\dfrac{1}{RT}\displaystyle\int_{p^{ref}}^{P}V_i^l\,dp\right)$	p^{ref} defined by the p^{ref} option code of HNRYPC
				
				$p_A^{*,l}$ Model name (if needed for p^{ref}
				
				p^{ref} Option code
				
				1: $p^{ref}=0$
				
				2: $p^{ref}=1$ atm
				
				3: $p^{ref}=p_A^{*,l}$ (T)
				  (Default = 2)
				
				V_i^{∞} Model name
				Integration code
				  (Default: 1 point)

		2	Specified model	θ_{iA}^{∞} Model name

Solid Fugacity Coefficient Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\varphi_i^{*,s}$ PHIS	Major	1	Specified Model	$\varphi_i^{*,s}$ Model name
		2	$\varphi_i^{*,v}\left(T, p_i^{*,s}\right) p_i^{*,s} \dfrac{\theta_i^{*,s}}{p}$	$p_i^{*,s}$ 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
$\theta_i^{*,s}$ PHISPC	Subord.	1	$\exp\left(\dfrac{1}{RT} \displaystyle\int_{p^{*,s}}^{p} V_i^{*,s}\, dp\right)$	$p_i^{*,s}$ Model name $V_i^{*,s}$ Model name Integration option code (Default: 1 point)
		2	Specified model	$\theta_i^{*,s}$ Model name
φ_i^{s} PHISMX	Major	1	Specified model	φ_i^{s} Model name
		2	$\varphi_i^{s} = f\left(x_i^{s}, \varphi_i^{*,s}\right)$	$\varphi_i^{*,s}$ Route ID φ_i^{s} Model name
		3	$\gamma_i^{s}\varphi_i^{*,s}$	γ_i^{s} Model name $\varphi_i^{*,s}$ Route ID

Vapor Enthalpy Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$H_i^{*,v}$ HV	Major	1	Specified model	$H_i^{*,v}$ Model name
		2	$H_i^{*,ig} + \left(H_i^{*,v} - H_i^{*,ig} \right)$	$\left(H_i^{*,v} - H_i^{*,ig} \right)$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig} = 0$)
		3	$H_i^{*,l} + \Delta_{vap} H_i^{*}$	$H_i^{*,l}$ Route ID $\Delta_{vap} H_i^{*}$ Model name
$H_i^{*,v} - H_i^{*,ig}$ DHV	Subord.	1	Specified model	$\left(H_i^{*,v} - H_i^{*,ig} \right)$ Model name
		2	$-RT^2 \left(\dfrac{\partial \ln \varphi_i^{*,v}}{\partial T} \right)$	$\varphi_i^{*,v}$ Model name
H_m^{v} HVMX	Major	1	Specified model	H_m^{v} Model name
		2	$\displaystyle\sum_i y_i H_i^{*,v}$	$H_i^{*,v}$ Route ID
		3	$H_m^{ig} + \left(H_m^{v} - H_m^{ig} \right)$	$\left(H_m^{v} - H_m^{ig} \right)$ Route ID (Default: $H_m^{v} - H_m^{ig} = 0$)
$H_m^{v} - H_m^{ig}$ DHVMX	Subord.	1	Specified model	$\left(H_m^{v} - H_m^{ig} \right)$ Model name
		2	$-RT^2 \displaystyle\sum_i y_i \left(\dfrac{\partial \ln \varphi_i^{v}}{\partial T} \right)$	φ_i^{v} Model name
		3	$H_m^{v} - H_m^{ig} = f(\gamma_i)$	γ_i Model name Equation of state model name

Liquid Enthalpy Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$H_i^{*,l}$ HL	Major	1	Specified model	$H_i^{*,l}$ Model name
		2	$H_i^{*,ig} + \left(H_i^{*,l} - H_i^{*,ig} \right)$	$\left(H_i^{*,l} - H_i^{*,ig} \right)$ Route ID
$H_i^{*,l} - H_i^{*,ig}$ DHL	Subord.	1	Specified model	$\left(H_i^{*,l} - H_i^{*,ig} \right)$ Model name
		2	$-RT^2 \left(\dfrac{\partial \ln \varphi_i^{*,l}}{\partial T} \right)$	$\varphi_i^{*,l}$ Model name
		3	$\left(H_i^{*,v}(T, p_i^{*,l}) - H_i^{*,ig}(T) \right) - \Delta_{vap} H_i^{*}(T)$ $+ \left(H_i^{*,l}(T,p) - H_i^{*,l}(T, p_i^{*,l}) \right)$	p_i^{l} Model name $\left(H_i^{*,v} - H_i^{*,ig} \right)$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) $\Delta_{vap} H_i^{l}$ Model name $\left(H_i^{*,l}(T,p) - H_i^{*,l}(T,p_i^{*,l}) \right)$ Route ID (Default: $H_i^{*,l}(T,p) - H_i^{*,l}(T,p_i^{*,l}) = 0$)
$H_i^{*,l}(T,p) -$ $H_i^{*,l}(T,p_i^{*,l})$ DHLPC	Subord.	1	$\left(H_i^{*,l}(T,p) - H_i^{*,ig}(T) \right) -$ $\left(H_i^{*,l}(T,p_{pi}^{*,l}) - H_i^{*,ig}(T) \right)$	$p_i^{*,l}$ Model name $\left(H_i^{*,l} - H_i^{*,ig} \right)$ Route ID
		2	$\displaystyle\int_{p_i}^{p} \left[V_i^{*,l} - T \left(\frac{\partial V_i^{*,l}}{\partial T} \right)_p \right] dp$	$p_i^{*,l}$ Model name $V_i^{*,l}$ Model name Integration option code (Default: 1 point)
		3	Specified model	$\left(H_i^{*,l}(T,p) - H_i^{*,l}(T,p_i^{*,l}) \right)$ Model name
H_m^{l} HLMX	Major	1	Specified model	H_m^{l} Model name

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
		2	$\sum_i x_i H_i^{*,l} + H_m^{E,l}$	$H_i^{*,l}$ Route ID $H_i^{E,l}$ Route ID (Default: $H_i^{E,l}=0$)
		3	$H_m^{ig} + \left(H_m^{l} - H_m^{ig}\right)$	$\left(H_m^{l} - H_m^{ig}\right)$ Route ID
		4	Electrolyte model $\left(x^t\right)$	H_m^{l} Model name x^t Route ID
$H_m^{l} - H_m^{ig}$ DHLMX	Subord.	1	Specified model	$\left(H_m^{l} - H_m^{ig}\right)$ Model name
		2	$\sum_i x_i \left(H_i^{*,l} - H_i^{*,ig}\right) + H_m^{E,I}$	$\left(H_i^{*,l} - H_i^{*,ig}\right)$ Route ID $H_m^{E,l}$ Route ID (Default: $H_m^{E,l} = 0$)
		3	Unsymmetric convention For subcritical components A or B: $\sum_i x_A \left(H_A^{*,I} - H_A^{*,ig}\right) + H_m^{E,I}$ $H_m^{E,I} = -RT^2 \sum_B x_B \left(\dfrac{\partial \ln \gamma_B}{\partial T}\right)$ For supercritical component i or j: $-RT^2 \sum_j x_j \left(\dfrac{\partial \ln \varphi_j^{I}}{\partial T}\right)$ where: $\varphi_\iota^{I} = \gamma_i \left(\dfrac{H_i}{p\gamma_i^{\infty}}\right)$ $\ln\left(\dfrac{H_i}{\gamma_\iota^{\infty}}\right) = \sum B\omega_B \ln\left(\dfrac{H_{iB}}{\gamma_{\iota B}^{\infty}}\right)$ $\ln = \lim_{\sum_i x_i \to 0}\left(\ln \gamma_\iota\right)$ $\sum_B w_B = 1$	$\left(H_A^{*,I} - H_A^{*,ig}\right)$ Route ID where: γ_B Model name H_{iB} Route ID w_B Model name w_B Model option code (see Model Option Code Help)

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
		4	Special mixing rule for Polymers Plus $$\sum_i x_i \left(H_i^{*,l} - H_i^{*,ig} \right) -$$ $$RT^2 \sum_i x_i \left(\frac{M_i}{M_i^t} \right) \left(\frac{\partial \ln \gamma_i}{\partial T} \right)$$	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
		5	Unsymmetric convention for Polymers Plus For subcritical components A or B: $$\sum_i x_A \left(H_A^{*,I} - H_A^{*,ig} \right) + H_m^{E,I}$$ $$H_m^{E,I} = -RT^2 \sum_B x_B \left(\frac{M_i}{M_i^t} \right) \left(\frac{\partial \ln \gamma_B}{\partial T} \right)$$ For supercritical component i or j: $$-RT^2 \sum_j x_j \left(\frac{\partial \ln \varphi_j^I}{\partial T} \right)$$ where: $$\varphi_\iota^I = \gamma_i \left(\frac{H_i}{p \gamma_i^\infty} \right)$$ $$\ln \left(\frac{H_i}{\gamma_\iota^\infty} \right) = \sum B \omega_B \ln \left(\frac{H_{iB}}{\gamma_{\iota B}^\infty} \right)$$ $$\ln = \lim_{\sum_i x_i \to 0} \left(\ln \gamma_\iota \right)$$ $$\sum_B w_B = 1$$	$\left(H_A^{*,I} - H_A^{*,ig} \right)$ 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 (see Model Option Code Help)
$H_m^{E,l}$ HLXS	Subord.	1	Specified model	$H_m^{E,l}$ Model name
		2	$$H_m^{E,l} = -RT^2 \sum_i x_i \left(\frac{\partial \ln \gamma_i}{\partial T} \right)$$	γ_i Model name
		3	Method for Polymers Plus 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

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$H_i^{*,s}$ HS	Major	1	Specified model	$H_i^{*,s}$ Model name
		2	$H_i^{*,ig} + \left(H_i^{*,s} - H_i^{*,ig} \right)$	$\left(H_i^{*,s} - H_i^{*,ig} \right)$ Route ID
$H_i^{*,s} - H_i^{*,ig}$ DHS	Subord.	1	Specified model	$\left(H_i^{*,s} - H_i^{*,ig} \right)$ Model name
		2	$\left(H_i^{*,v}\left(T, p_i^{*,s}\right) - H_i^{*,g}(T)\right) - \Delta_{sub}H_i^*(T)$ $+\left(H_i^{*,s}(T,p) - H_i^{*,s}\left(T, p_i^{*,s}\right)\right)$	$p_i^{*,s}$ Model name $\left(H_i^{*,v} - H_i^{*,ig} \right)$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) $\Delta_{sub}H_i^*(T)$ Model name $\left(H_i^{*,s}(T,p) - H_i^{*,s}\left(T, p_i^{*,s}\right)\right)$ Route ID (Default: $H_i^{*,s}(T,p) - H_i^{*,s}\left(T, p_i^{*,s}\right) = 0$)
$H_i^{*,s}(T,p) -$ $H_i^{*,s}\left(T, p_i^{*,s}\right)$ DHSPC	Subord.	1	$\int\limits_p^p \left[V_i^{*,s} - T\left(\dfrac{\partial V_i^{*,s}}{\partial T} \right) \right] dp$	$p_i^{*,s}$ Model name $V_i^{*,s}$ Model name Integration option code (Default: 1 point)
H_m^s HSMX	Major	1	Specified model	Model name
		2	$\sum_i x_i^s H_i^{*,s} + H_m^{E,s}$	H_m^s Route ID $H_i^{*,s}$ Route ID $H_m^{E,s}$ (Default: $H_m^{E,s} = 0$)
		3	$H_m^{ig} + \left(H_m^s - H_m^{ig} \right)$	$\left(H_m^s - H_m^{ig} \right)$ Route ID
$H_m^s - H_m^{ig}$ DHSMX	Subord.	1	Specified model	$\left(H_m^s - H_m^{ig} \right)$ Model name
		2	$\sum_i x_i^s \left(H_i^{*,s} - H_i^{*,ig} \right) + H_m^{E,s}$	$\left(H_i^{*,s} - H_i^{*,ig} \right)$ Route ID $H_m^{E,s}$ Route ID (Default: $H_m^{E,s} = 0$)

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$H_m^{E,s}$ HSXS	Subord.	1	Specified model	$H_m^{E,s}$ Model name
		2	$H_m^{E,s} = -RT^2 \sum_i x_i^s \left(\dfrac{\partial \ln \gamma_i^s}{\partial T} \right)$	γ_i Model name

Vapor Gibbs Energy Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\mu_i^{*,v}$ GV	Major	1	Specified model	$\mu_i^{*,v}$ Model name
		2	$\mu_i^{*,ig} + \left(\mu_i^{*,v} - \mu_i^{*,ig} \right)$	$\left(\mu_i^{*,v} - \mu_i^{*,ig} \right)_{\text{Route ID}}$ (Default: $\mu_i^{*,v} - \mu_i^{*,ig} = 0$)
$\mu_i^{*,v} - \mu_i^{*,ig}$ DGV	Subord.	1	Specified model	$\left(\mu_i^{*,v} - \mu_i^{*,ig} \right)_{\text{Model name}}$
		2	$RT \ln \varphi_i^{*,v} + RT \ln \left(\dfrac{p}{p^{ref}} \right)$	$\varphi_i^{*,v}$ Route ID
G_m^v GVMX	Major	1	Specified model	G_m^v Model name
		2	$\sum_i y_i \mu_i^{*,v} + RT \sum_i y_i \ln y_i$	$\mu_i^{*,v}$ Route ID
		3	$G_m^{ig} + \left(G_m^v - G_m^{ig} \right)$	$\left(G_m^v - G_m^{ig} \right)_{\text{Route ID}}$ (Default: $G_m^v - G_m^{ig} = 0$)
$G_m^v - G_m^{ig}$ DGVMX	Subord.	1	Specified model	$\left(G_m^v - G_m^{ig} \right)_{\text{Model name}}$
		2	$RT \sum_i y_i \ln \varphi_i^v + RT \ln \left(\dfrac{p}{p^{ref}} \right)$	φ_i^v Route ID (Default: $\varphi_i^v = 1$)
		3	$G_m^v - G_m^{ig} = f(\gamma_i)$	γ_i Model name Equation of state model name

Liquid Gibbs Energy Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\mu_i^{*,l}$ GL	Major	1	Specified model	$\mu_i^{*,l}$ Model name
		2	$\mu_i^{*,ig} + \left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$	$\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$ Route ID
$\mu_i^{*,l} - \mu_i^{*,ig}$ DGL	Subord.	1	Specified model	$\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$ Model name
		2	$RT\ln\varphi^{*,l} + RT\ln\left(\dfrac{p}{p^{ref}}\right)$	$\varphi_i^{*,l}$ Route ID
		3	$\left(\mu_i^{*,l}\left(T,p_i^{*,l}\right) - \mu_i^{*,ig}(T)\right) +$ $\left(\mu_i^{*,l}(T,p) - \mu_i^{*,l}\left(T,p_i^{*,l}\right)\right)$	$p_i^{*,l}$ Model name $\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$ Route ID (Default: $\mu_i^{*,l} - \mu_i^{*,ig} = 0$) $\left(\mu_i^{*,l}(T,p) - \mu_i^{*,l}\left(T,p_i^{*,l}\right)\right)$ Route ID (Default: $\mu_i^{*,l}(T,p) - \mu_i^{*,l}\left(T,p_i^{*,l}\right) = 0$)
$\mu_i^{*,l}(T,p) -$ $\mu_i^{*,l}\left(T,p_i^{*,l}\right)$ DGLPC	Subord.	1	$\left(\mu^{*,l}(T,p) - \mu_i^{*,ig}(T)\right) -$ $\left(\mu_i^{*,l}\left(T,p_i^{*,l}\right) - \mu_i^{*,ig}(T)\right)$	$p_i^{*,l}$ Model name $\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$ Route ID
		2	$\displaystyle\int_{p_i^{*,l}}^{p} V_i^{*,l}\,dp$	$p_i^{*,l}$ Model name $V_i^{*,l}$ Model Name Integration option code (Default: 1 point)
G_m^l GLMX	Major	1	Specified model	G_m^l Model name
		2	$\displaystyle\sum_i x_i\mu_i^{*,l} +$ $RT\displaystyle\sum_i x_i\ln x_i + G_m^{E,l}$	$\mu_i^{*,l}$ Route ID $G_m^{E,l}$ Route ID (Default: $G_m^{E,l} = 0$)
		3	$G_m^{ig} + \left(G_m^l - G_m^{ig}\right)$	
		4	$\left(x^t\right)$	Model name x^t Route ID

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$G_m^l - G_m^{ig}$ DGLMX	Subord.	1	Specified model	$\left(G_m^l - G_m^{ig}\right)$ Model name
		2	$\displaystyle\sum_i x_i \left(\mu_i^{*,l} - \mu_i^{*,ig}\right) + G_m^{E,l}$	$\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$ Route ID $G_m^{E,l}$ Route ID (Default: $G_m^{E,l} = 0$)
		3	$\displaystyle RT \sum_i x_i \ln \varphi_i^l +$ $RT \ln\left(\dfrac{p}{p^{ref}}\right)$	φ_i^l Route ID
		4	$G_m^l - G_m^{ig} = f(\gamma_i)$	γ_i Model name Equation of state model name
$G_m^{E,l}$ GLXS	Subord.	1	Specified model	$G_m^{E,l}$ Model name
		2	$\displaystyle RT \sum_i x_i \ln \gamma_i$	γ_i Model name

Solid Gibbs Energy Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\mu_i^{*,s}$ GS	Major	1	Specified model	$\mu_i^{*,s}$ Model name
		2	$\mu_i^{*,ig} + \left(\mu_i^{*,s} - \mu_i^{*,ig}\right)$	$\left(\mu_i^{*,s} - \mu_i^{*,ig}\right)_{\text{Route ID}}$
$\mu_i^{*,s} - \mu_i^{*,ig}$ DGS	Subord.	1	Specified model	$\left(\mu_i^{*,s} - \mu_i^{*,ig}\right)_{\text{Model name}}$
		2	$RT\ln\varphi^{*,s} + RT\ln\left(\dfrac{p}{p^{ref}}\right)$	$\varphi_i^{*,s}$ Route ID
		3	$\left(\mu_i^{*,s}\left(T, p_i^{*,s}\right) - \mu_i^{*,ig}(T)\right) +$ $\left(\mu_i^{*,s}(T,p) - \mu_i^{*,s}\left(T, p_i^{*,s}\right)\right)$	$p_i^{*,s}$ Model name $\left(\mu_i^{*,s}\left(T, p_i^{*,s}\right) - \mu_i^{*,ig}(T)\right)_{\text{Route ID}}$ (Default: $\mu_i^{*,s}\left(T, p_i^{*,s}\right) - \mu_i^{*,ig}(T) = 0$) $\left(\mu_i^{*,s}(T,p) - \mu_i^{*,s}\left(T, p_i^{*,s}\right)\right)_{\text{Route ID}}$ (Default: $\mu_i^{*,s}(T,p) - \mu_i^{*,s}\left(T, p_i^{*,s}\right) = 0$)
$\mu_i^{*,s}(T,p) - \mu_i^{*,s}\left(T, p_i^{*,s}\right)$ DGSPC	Subord.	1	$\displaystyle\int_{p_i^{*,l}}^{p} V_i^{*,l}\, dp$	$p_i^{*,l}$ Model name $V_i^{*,l}$ Model Name Integration option code (Default: 1 point)
G_m^s GSMX	Major	1	Specified model	G_m^s Model name
		2	$\displaystyle\sum_i x_i^s \mu_i^{*,s} + G_m^{E,s} +$ $RT\displaystyle\sum_i x_i^s \ln x_i^s$	$\mu_i^{*,s}$ Route ID $G_m^{E,s}$ Route ID (Default: $G_m^{E,s} = 0$)
		3	$G_m^{ig} + \left(G_m^s - G_m^{ig}\right)$	
$G_m^s - G_m^{ig}$ DGSMX	Subord.	1	Specified model	$\left(G_m^s - G_m^{ig}\right)_{\text{Model name}}$

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
		2	$\sum_i x_i^s \left(\mu_i^{*,s} - \mu_i^{*,ig} \right) + G_m^{E,s}$	$\left(\mu_i^{*,s} - \mu_i^{*,ig} \right)_{\text{Route ID}}$ $G_m^{E,s}$ Route ID (Default: $G_m^{E,s} = 0$)
$G_m^{E,s}$ GSXS	Subord.	1	Specified model	$G_m^{E,s}$ Model name
		2	$RT \sum_i x_i^s \ln \gamma_i^s$	γ_i Model name

Vapor Entropy Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$S_i^{*,v}$ SV	Major	1	$\dfrac{1}{T}\left(H_i^{*,v} - \mu_i^{*,v}\right)$	$H_i^{*,v}$ Route ID
		2	$S_i^{*,ig} + \left(S_i^{*,v} - S_i^{*,ig}\right)$	$\left(S_i^{*,v} - S_i^{*,ig}\right)$ Route ID (Default: $S_i^{*,v} - S_i^{*,ig} = 0$)
		3	Specified model	$S_i^{*,v}$ Model name
$S_i^{*,v} - S_i^{*,ig}$ DSV	Subord.	1	$\left(\dfrac{H_i^{*,v} - H_i^{*,ig}}{T}\right) -$ $\left(\dfrac{\mu_i^{*,v} - \mu_i^{*,ig}}{T}\right)$	$\left(H_i^{*,v} - H_i^{*,ig}\right)$ Route ID (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) $\left(\mu_i^{*,v} - \mu_i^{*,ig}\right)$ Route ID (Default: $\mu_i^{*,v} - \mu_i^{*,ig} = 0$)
		2	$-\dfrac{\partial}{\partial T}\left(\mu_i^{*,v} - \mu_i^{*,ig}\right)$	$\left(\mu_i^{*,v} - \mu_i^{*,ig}\right)$ Model name
S_m^{v} SVMX	Major	1	$\dfrac{1}{T}\left(H_m^{v} - G_m^{v}\right)$	H_m^{v} Route ID G_m^{v} Route ID
		2	$S_m^{ig} + \left(S_m^{v} - S_m^{ig}\right)$	$\left(S_m^{v} - S_m^{ig}\right)$ Route ID (Default: $S_m^{v} - S_m^{ig} = 0$)
		3	Specified model	S_m^{v} Model name
$S_m^{v} - S_m^{ig}$ DSVMX	Subord.	1	Specified model	$\left(S_m^{v} - S_m^{ig}\right)$ Model name
		2	$\left(\dfrac{H_m^{v} - H_m^{ig}}{T}\right) - \left(\dfrac{G_m^{v} - G_m^{ig}}{T}\right)$	$\left(H_m^{v} - H_m^{ig}\right)$ Route ID (Default: $H_m^{v} - H_m^{ig} = 0$) $\left(G_m^{v} - G_m^{ig}\right)$ Route ID (Default $G_m^{v} - G_m^{ig} = 0$)
		3	$-\dfrac{\partial}{\partial T}\left(G_m^{v} - G_m^{ig}\right)$	$\left(G_m^{v} - G_m^{ig}\right)$ Model name
		4	$S_m^{v} - S_m^{ig} = f(\gamma_i)$	γ_i Model name Equation of state model name

Liquid Entropy Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$S_i^{*,l}$ SL	Major	1	$\dfrac{1}{T}\left(H_i^{*,l} - \mu_i^{*,l}\right)$	$H_i^{*,l}$ Route ID $\mu_i^{*,l}$ Route ID
		2	$S_i^{*,ig} + \left(S_i^{*,v} - S_i^{*,ig}\right)$	$\left(S_i^{*,l} - S_i^{*,ig}\right)$ Route ID
		3	Specified model	$S_i^{*,l}$ Model name
$S_i^{*,l} - S_i^{*,ig}$ DSL	Subord.	1	$\left(\dfrac{H_i^{*,l} - H_i^{*,ig}}{T}\right) - \left(\dfrac{\mu_i^{*,l} - \mu_i^{*,ig}}{T}\right)$	$\left(H_i^{*,l} - H_i^{*,ig}\right)$ Route ID
		2	$-\dfrac{\partial}{\partial T}\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$	$\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$ Route ID $\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$ Model name
		3	Specified Model	$\left(S_i^{*,l} - S_i^{*,ig}\right)$ Model name
S_m^{l} SLMX	Major	1	$\dfrac{1}{T}\left(H_m^{l} - G_m^{l}\right)$	H_m^{l} Route ID G_m^{l} Route ID
		2	$S_m^{ig} + \left(S_m^{l} - S_m^{ig}\right)$	$\left(S_m^{l} - S_m^{ig}\right)$ Route ID
		3	Specified model	S_m^{l} Model name
		4	$S_m^{l} = f\left(H_m^{l}, G_m^{l}, x^t\right)$	H_m^{l} model G_m^{l} model x^t Route ID
$S_m^{l} - S_m^{ig}$ DSLMX	Subord.	1	Specified model	$\left(S_m^{l} - S_m^{ig}\right)$ Model name
		2	$\left(\dfrac{H_m^{l} - H_m^{ig}}{T}\right) - \left(\dfrac{G_m^{l} - G_m^{ig}}{T}\right)$	$\left(H_m^{l} - H_m^{ig}\right)$ Route ID $\left(G_m^{l} - G_m^{ig}\right)$ Route ID
		3	$-\dfrac{\partial}{\partial T}\left(G_m^{l} - G_m^{ig}\right)$	$\left(G_m^{l} - G_m^{ig}\right)$ Model name
		4	$S_m^{l} - S_m^{ig} = f(\gamma_i)$	γ_i Model name Equation of state model name

Solid Entropy Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$S_i^{*,s}$ SS	Major	1	Specified model	$S_i^{*,s}$ Model name
		2	$\dfrac{1}{T}\left(H_i^{*,s} - \mu_i^{*,s}\right)$	$H_i^{*,s}$ Route ID $\mu_i^{*,s}$ Route ID
$S_i^{*,s} - S_i^{*,ig}$ DSS	Subord.	1	$\left(\dfrac{H_i^{*,s} - H_i^{*,ig}}{T}\right) - \left(\dfrac{\mu_i^{*,s} - \mu_i^{*,ig}}{T}\right)$	$\left(H_i^{*,s} - H_i^{*,ig}\right)$ Route ID $\left(\mu_i^{*,s} - \mu_i^{*,ig}\right)$ Route ID
		2	Specified model	$\left(S_i^{*,s} - S_i^{*,ig}\right)$ Model name
S_m^{s} SSMX	Major	1	$\dfrac{1}{T}\left(H_m^{s} - G_m^{s}\right)$	H_m^{s} Route ID G_m^{s} Route ID
		2	$S_m^{ig} + \left(S_m^{s} - S_m^{ig}\right)$	$\left(S_m^{s} - S_m^{ig}\right)$ Route ID
$S_m^{s} - S_m^{ig}$ DSSMX	Subord.	1	Specified model	$\left(S_m^{s} - S_m^{ig}\right)$ Model name
		2	$\left(\dfrac{H_m^{s} - H_m^{ig}}{T}\right) - \left(\dfrac{G_m^{s} - G_m^{ig}}{T}\right)$	$\left(H_m^{s} - H_m^{ig}\right)$ Route ID $\left(G_m^{s} - G_m^{ig}\right)$ Route ID
		3	$-\dfrac{\partial}{\partial T}\left(G_m^{s} - G_m^{ig}\right)$	$\left(G_m^{s} - G_m^{ig}\right)$ Model name

Molar Volume Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$V_i^{*,v}$ VV	Major	1	Specified model	$V_i^{*,v}$ Model name
V_m^v VVMX	Major	1	Specified model	V_m^v Model name
		2	$V_m^v = f\left(y_i, V_i^{*,v}\right)$	$V_i^{*,v}$ Route ID V_m^v Model name
		3	$V_m^v = f\left(\gamma_i\right)$	γ_i Model name V_m^v Model name (eos only)
$V_i^{*,l}$ VL	Major	1	Specified model	$V_i^{*,l}$ Model name
V_m^l VLMX	Major	1	Specified model	V_m^l Model name
		2	$V_m^l = f\left(x_i, V_i^{*,l}\right)$	$V_i^{*,l}$ Route ID V_m^l Model name
		3	Electrolyte model $\left(x^t\right)$	$V_i^{*,l}$ Model name x^t Route ID
		4	$V_m^l = f\left(\gamma_i\right)$	γ_i Model name V_m^l Model name (eos only)
$V_i^{*,s}$ VS	Major	1	Specified model	$V_i^{*,s}$ Model name
V_m^s VSMX	Major	1	Specified model	V_m^s Model name
		2	$V_m^s = f\left(x_i^s, V_i^{*,s}\right)$	$V_i^{*,s}$ Route ID V_m^s Model name

Viscosity Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$n_i^{*,v}$ MUV	Major	1	Specified model	$\eta_i^{*,v}$ Model name
		2	$\eta_i^{*,v} = \eta_i^{*,v}(p=0)$	$\left(\eta_i^{*,v}(p=0)\right)_{\text{Route ID}}$
		3	$\eta_i^{*,v} = f\left(V_i^{*,v}\right)$	$V_i^{*,v}$ Route ID $\eta_i^{*,v}$ Model name
		4	$\eta_i^{*,v} = \eta_i^{*,v}(p=0)$ $+ \left(\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0)\right)$	$\left(\eta_i^{*,v}(p=0)\right)_{\text{Route ID}}$ $\left(\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0)\right)_{\text{Route ID}}$
$\eta_i^{*,v}(p=0)$ MUVLP	Subord.	1	Specified model	$\left(\eta_i^{*,v}(p=0)\right)_{\text{Model name}}$
$\left(\begin{array}{c}\eta_i^{*,v}(p)- \\ \eta_i^{*,v}(p=0)\end{array}\right)$ MUVPC	Subord.	1	Specified model	$\left(\eta_i^{*,v}(p) - \eta_o^{*,v}(p=0)\right)_{\text{Model name}}$
		2	$\left(\eta_i^{*,v}(p) - \eta_o^{*,v}(p=0)\right) = f\left(V_i^{*,v}\right)$	$V_i^{*,v}$ Route ID Model name
n^v MUVMX	Major	1	Specified model	η^v Model name
		2	$\eta^v = f\left(y_i, \eta_i^{*,v}\right)$	$\eta_i^{*,v}$ Route ID η^v Model name
		3	$\eta^v = \eta^v(p=0)$	$\left(\eta^v(p=0)\right)_{\text{Route ID}}$
		4	$\eta^v = f\left(V_m^v\right)$	V_m^v Route ID
		5	$\eta_i^v = \eta_i^v(p=0)+$ $\left(\eta_i^v(p) - \eta_i^v(p=0)\right)$	η^v Model name $\left(\eta^v(p=0)\right)_{\text{Route ID}}$ $\left(\eta_i^v(p) - \eta_i^v(p=0)\right)_{\text{Route ID}}$
$\left(\eta^v(p=0)\right)$ MUVMXLP	Subord.	1	Specified model	$\left(\eta^v(p=0)\right)_{\text{Model name}}$
		2	$\left(\eta^v(p=0)\right) = f\left(y_i, \eta_i^{*,v}(p=0)\right)$	$\left(\eta_i^{*,v}(p=0)\right)_{\text{Route ID}}$ $\left(\eta^v(p=0)\right)_{\text{Model name}}$

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\left(\begin{array}{c}\eta^v(p)- \\ \eta^v(p=0)\end{array}\right)$ MUVMXPC	Subord.	1	Specified model	$\left(\eta^v(p)-\eta^v(p=0)\right)$Model name
		2	$\left(\eta^v(p)-\eta^v(p=0)\right)=f\left(V_m^v\right)$	V_m^v Route ID $\left(\eta^v(p)-\eta^v(p=0)\right)$Model name
$\eta_i^{*,l}$ MUL	Major	1	Specified model	$\eta_i^{*,l}$ Model name
		2	$\eta_i^{*,l}=f\left(V_i^{*,l}\right)$	$V_i^{*,l}$ Route ID $\eta_i^{*,l}$ Model Name
η^l MULMX	Major	1	Specified model	η^l Model name
		2	$\eta^l=f\left(x_i,\eta_i^{*,l}\right)$	$\eta_i^{*,l}$ Route ID η^l Model name
		3	$\eta^l=f\left(V_m^l\right)$	V_m^l Route ID η^l Model name
		4	Electrolyte model $\left(x^t\right)$	η^l Model name x^t Route ID

Thermal Conductivity Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\lambda_i^{*,v}$ KV	Major	1	Specified model	$\lambda_i^{*,v}$ Model name
		2	$\lambda_i^{*,v} = \left(\lambda_i^{*,v}(p=0)\right)$	$\left(\lambda_i^{*,v}(p=0)\right)_{\text{Route ID}}$
		3	$\lambda_i^{*,v} = \lambda_i^{*,v}(p=0)$ $\quad + \left(\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p=0)\right)$	$\left(\lambda_i^{*,v}(p=0)\right)_{\text{Route ID}}$ $\left(\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p=0)\right)_{\text{Route ID}}$
		4	$\lambda_i^{*,v} = f\left(V_i^{*,v}, \eta_i^{*,v}(p=0)\right)$	$V_i^{*,v}$ Route ID $\eta_i^{*,v}(p=0)$ Model name $\lambda_i^{*,v}$ Model Name
$\lambda_i^{*,v}(p=0)$ KVLP	Subord.	1	Specified model	$\lambda_i^{*,v}(p=0)$ Model name
		2	$\lambda_i^{*,v}(p=0) = f\left(\eta_i^{*,v}(p=0)\right)$	$\eta_i^{*,v}(p=0)$ Route ID $\lambda_i^{*,v}$ Model name
$\lambda_i^{*,v}(p) -$ $\lambda_i^{*,v}(p=0)$ KVPC	Subord.	1	Specified model	$\left(\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p=0)\right)_{\text{Model name}}$
		2	$\left(\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p=0)\right) = f\left(V_i^{*,v}\right)$	$V_i^{*,v}$ Route ID $\left(\lambda_i^{*,v}(p) - \lambda_i^{*,v}(p=0)\right)_{\text{Model name}}$
λ^v KVMX	Major	1	Specified model	λ^v Model name
		2	$\lambda^v = f\left(y_i, \lambda_i^{*,v}\right)$	$\lambda_i^{*,v}$ Route ID λ^v Model name
		3	$\lambda^v = \lambda^v(p=0)$	$\left(\lambda^v(p=0)\right)_{\text{Route ID}}$
		4	$\lambda^v = \lambda^v(p=0) +$ $\quad \left(\lambda^v(p) - \lambda^v(p=0)\right)$	$\left(\lambda^v(p=0)\right)_{\text{Route ID}}$ $\left(\lambda^v(p) - \lambda^v(p=0)\right)_{\text{Route ID}}$
		5	$\lambda^v = f\left(V_m^v, \eta^v(p=0)\right)$	V_m^v Route ID $\left(\eta^v(p=0)\right)_{\text{Route ID}}$ λ^v Model name

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\lambda^{v}(p=0)$ KVMXLP	Subord.	1	Specified model	$\left(\lambda^{v}(p=0)\right)_{\text{Model name}}$
		2	$\lambda^{v}(p=0) = f\left(y_i, \lambda_i^{*,v}(p=0), \eta_i^{*,v}(p=0)\right)$	$\lambda_i^{*,v}{}_{\text{Route ID}}$ $\eta_i^{*,v}(p=0)_{\text{Route ID}}$ $\left(\lambda^{v}(p=0)\right)_{\text{Model name}}$
$\lambda^{v}(p) - \lambda^{v}(p=0)$ KVMXPC	Subord.	1	Specified model	$\left(\lambda^{v}(p) - \lambda^{v}(p=0)\right)_{\text{Model name}}$
		2	$\left(\lambda^{v}(p) - \lambda^{v}(p=0)\right) = f\left(V_m^{v}\right)$	$V_m^{v}{}_{\text{oute ID}}$ $\left(\lambda^{v}(p) - \lambda^{v}(p=0)\right)_{\text{Model name}}$
$\lambda_i^{*,l}$ KL	Major	1	Specified model	$\lambda_i^{*,l}{}_{\text{Model name}}$
		2	$\lambda_i^{*,l} = f\left(V_i^{*,l}, \eta_i^{*,v}(p=0)\right)$	$V_i^{*,l}{}_{\text{Route ID}}$ $\left(\eta_i^{*,v}(p=0)\right)_{\text{Route ID}}$ $\lambda_i^{*,l}{}_{\text{Model name}}$
λ^{l} KLMX	Major	1	Specified model	$\lambda^{l}{}_{\text{Model name}}$
		2	$\lambda^{l} = f\left(x_i, \lambda_i^{*,l}\right)$	$\lambda_i^{*,l}{}_{\text{Route ID}}$ $\lambda^{l}{}_{\text{Model name}}$
		3	$\lambda^{l} = f\left(V_m^{l}, \eta^{v}(p=0)\right)$	$V_m^{l}{}_{\text{Route ID}}$ $\left(\eta^{v}(p=0)\right)_{\text{Route ID}}$ $\lambda^{l}{}_{\text{Model name}}$
		4	Electrolyte model $\left(x^{t}\right)$	$\lambda^{l}{}_{\text{Model name}}$ $x^{t}{}_{\text{Route ID}}$
$\lambda_i^{*,s}$ KS	Major	1	Specified model	$\lambda_i^{*,s}{}_{\text{Model name}}$
λ^{s} KSMX	Major	1	Specified model	$\lambda^{s}{}_{\text{Model name}}$
		2	$\lambda^{s} = f\left(x_i^{s}, \lambda_i^{*,s}\right)$	$\lambda_i^{*,s}{}_{\text{Route ID}}$ $\lambda^{s}{}_{\text{Model name}}$

Diffusion Coefficient Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
D_{ij}^v DV	Major	1	Specified model	D_{ij}^v Model name
D_i^v DVMX	Major	1	Specified model	D_i^v Model name
		2	$D_i^v = f\left(y_i, D_{ij}^v\right)$	D_{ij}^v Route ID y_i Model name
D_{ij}^l DL	Major	1	Specified model	Model name
D_i^l DLMX	Major	1	Specified model	Model name
		2	$D_i^l = f\left(x_i, D_{ij}^l\right)$	D_{ij}^l Route ID D_i^l Model name
		3	$D_i^l = f\left(x_i, \eta^l\right)$	η^l Route ID D_i^l Model name
		4	Electrolyte model $\left(x^t\right)$	D_i^l Model name x^t Route ID

Surface Tension Methods

Property Symbol and Name	Property Type	Method Code	Method	Route Structure Information Required
$\sigma_i^{*,l}$ SIGL	Major	1	Specified model	Model name
σ^l SIGLMX	Major	1	Specified model	Model name
		2	$\sigma^l = f\left(x_i, \sigma_i^{*,l}\right)$	$\sigma_i^{*,l}$ Route ID σ^l Model name
		3	Electrolyte model $\left(x^t\right)$	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
Each property value needed for a method evaluation is obtained from either another method evaluation or a model evaluation. Properties obtained by method evaluation are major or subordinate properties. Properties obtained by a model evaluation are intermediate properties. The calculation of the top-level property is dictated by:

- Property name
- Method
- Sub-level route for each major or subordinate property
- Model name for each intermediate property (sometimes with a model option code)

This information is called a route. There is not necessarily a major or subordinate property in each method, but if one occurs in the method of the property of interest, then the route depends on sub-level routes. There can be any number of levels in a route. Each level needs the information listed previously to be completely specified. This way a tree of information is formed. Since a model does not depend on lower-level information, you can think of it as an end-point of a tree branch. Model option codes are discussed in Models. (Example 1 discusses a route that does *not* depend on other routes.)

Each built-in route in the Aspen Physical Property System has a unique route ID, which is composed of the property name (see the tables labeled Major Properties in the Aspen Physical Property System, Subordinate Properties in the Aspen Physical Property System, and Intermediate Properties in the Aspen Physical Property System) and a number, for example HLMX10. Therefore the route ID can be used to represent the route information. (See example 2 for a route which depends on a secondary route.)

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.

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 Property Methods Routes sheet shows the routes used in a property method. If you want to see all of the built-in routes used for calculating the property specified in the Property field, use the list box in a Route ID field (see the figure labeled Properties Property Methods Routes Sheet.

Properties Property Methods Routes Sheet

Example 1 shows route information for PHILMX, method 1. Example 2 shows Route information for HLMX, method 3.

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. The model can be an equation-of-state model, that calculates the fugacity coefficient as a function of state variables and correlation parameters:

$$\varphi_i^l = f(p, T, x_i, correlation\ parameters)$$

There are many models that can be used to calculate φ_i^l, such as the Redlich-Kwong-Soave model, the Peng-Robinson model, or 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:

$$H_m^l = H_m^{ig} + \left(H_m^l - H_m^{ig} \right)$$

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. 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, 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. Properties obtained by model evaluation are called intermediate properties. They never depend on major or subordinate properties, which need a method evaluation. In contrast to methods which are based on universal scientific principles only, models are much more arbitrary in nature, and have constants which need to be determined by data fitting. An example of a model is the Extended Antoine vapor pressure equation (see Chapter 3). 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 Properties Property Methods Models sheet displays the models that are globally used in the routes of the current property method (see the figure labeled Properties Property Methods Models Sheet). In specific routes, exceptions to the global usage may occur. Modifying and Creating Routes discusses how to identify these

exceptions. For a given model, click on the Affected Properties button to display a list of properties which are affected by the model calculations. Use the list box on the Model Name field to display a list of all available models for a specific property. You can also use the tables labeled Thermodynamic Physical Property Models , Transport Physical Property Models , and Nonconventional Solid Property Models on page . 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*.)

Properties Property 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 Property Methods Models sheet, first select the model, then click the Option Codes button to display a list of option code values for the model. Use Help for descriptions of the option codes.

*Thermodynamic Physical
Property Models*

Thermodynamic Properties Model	Model Name	Phase	Properties
Antoine/Wagner	PL0XANT	L L1 L2	PL
API liquid volume	VL2API	L	VLMX
Aqueous Electrolyte NRTL Enthalpy	HAQELC	L	HLMX
Aqueous Electrolyte NRTL Gibbs Energy	GAQELC	L	GLMX
ASME Steam Tables	ESH2O0,ESH2O	V L	†
Brelvi-O'Connell	VL1BROC	L	VLPM
Bromley-Pitzer	GMPT2	L	GAMMA
Bromley-Pitzer Enthalpy	HAQPT2	L	HLMX
Bromley-Pitzer Gibbs Energy	GAQPT2	L	GLMX
BWR-Lee-Starling	ESBWR0, ESCSTBWR	V L	†,††
Cavett Liquid Enthalpy Departure	DHL0CVT, DHL2CVT	L	DHL,DHLMX
Chao-Seader	PHL0CS	L	PHIL
Clarke Aqueous Electrolyte Density	VAQCLK	L	VLMX
Constant Activity Coefficient	GMCONS	S	GAMMA
Costald Liquid Volume	VL0CTD,VL2CTD	L	VL,VLMX
Debije-Hückel Volume	VAQDH	L	VLMX
DIPPR Liquid Heat Capacity	HL0DIP, DHL0DIP	L	HL, DHL
Electrolyte NRTL	GMENRTL	L L1 L2	GAMMA
Electrolyte NRTL Enthalpy	HMXENRTL	L	HLMX
Electrolyte NRTL Gibbs Energy	GMXENRTL	L	GLMX
Grayson-Streed	PHL0GS	L	PHIL
Hayden-O'Connell	ESHOC0, ESHOC	V	†,††
Henry's constant	HENRY1	L	HNRY,WHNRY
HF equation of state	ESHF0, ESHF	V	†,††
Ideal Gas	ESIG0, ESIG	V	†,††
Kent-Eisenberg	ESAMIN	L	PHILMX, GLMX, HLMX, SLMX
Lee-Kesler	ESLK	V L	†††
Lee-Kesler-Plöcker	ESLKP0, ESLKP	V L	†,††
Modified UNIFAC Dortmund	GMUFDMD	L L1 L2	GAMMA
NBS/NCR Steam Tables	ESSTEAM0, ESSTEAM	V L	†,††
Nothnagel	ESNTH0, ESNTH	V	†,††
NRTL (Non-Random Two Liquid)	GMRENON	L	GAMMA
Peng-Robinson-Boston-Mathias	ESPR0, ESPR	V L	†,††
Pitzer	GMPT1	L	GAMMA
Pitzer Enthalpy	HAQPT1	L	HLMX
Pitzer Gibbs Energy	GAQPT1	L	GLMX

Polynomial Activity Coefficient	GMPOLY	S	GAMMA
Predictive SRK	ESRKSV10, ESRKSV1	V L	†††
Peng-Robinson-Wong-Sandler	ESPRWS0, ESPRWS	V L	†††
Peng-Robinson-MHV2	ESPRV20, ESPRV2	V L	†††
Rackett / DIPPR Liquid Density	VL0RKT, VL2RKT	L	VL,VLMX
Redlich-Kister	GMREDKIS	L S	GAMMA
Redlich-Kwong	ESRK0, ESRK	V	†,††
Redlich-Kwong-Soave-Boston-Mathias	ESRKS0, ESRKS	V L	†,††
Redlich-Kwong-Aspen	ESRKA0, ESRKA	V L	†,††
RKS-MHV2	ESRKSV20, ESRKSV2	V L	†††
RKS-Wong-Sandler	ESRKWSWS0, ESRKSWS	V L	†††
Schwartzentruber-Renon	ESRKU0, ESRKU	V L	†,††
Scatchard-Hildebrand	GMXSH	L	GAMMA
Solids Heat Capacity Polynomial	HS0POLY	S	HS
Solids Volume Polynomial	VS0POLY	S	VS
Standard Peng-Robinson	ESPRSTD0, ESPRSTD	V L	†,††
Standard Redlich-Kwong-Soave	ESRKSTD0, ESRKSTD	V L	†,††
Three-Suffix Margules	GMMARGUL	L S	GAMMA
UNIFAC	GMUFAC	L L1 L2	GAMMA
UNIQUAC	GMUQUAC	L L1 L2	GAMMA
Van Laar	GMVLAAR	L	GAMMA
Wagner interaction parameter	GMWIP	S	GAMMA
Watson / DIPPR	DHVLWTSN	L	DHVL
Wilson	GMWILSON	L	GAMMA

†   *A pure component equation-of-state model calculates:*
PHIL,PHIV,DHL,DHV,DGL,DGV,DSL,DSV,VL,VV

††   *A mixture equation-of-state model calculates:*
PHILMX,PHIVMX,DHLMX,DHVMX,DGLMX,DGVMX,DSLMX,DSVMX,VLMX,VVMX

†††   *DHLMX,DHVMX,DGLMX,DGVMX,DSLMX,DSVMX,VLMX,VVMX*

Transport Property Models

Thermodynamic Properties Model	Model Name	Phase	Properties
Andrade / DIPPR	MUL0ANDR, MUL2ANDR	L	MUL, MULMX
API liquid viscosity	MUL2API	L	MULMX
API surface tension	SIG2API	L	SIGLMX
Chapman-Enskog-Brokaw / DIPPR	MUV0CEB	V	MUVLP
Chapman-Enskog-Brokaw mixing rule	MUV2CEB	V	MUVMXLP
Chapman-Enskog-Wilke-Lee Binary	DV0CEWL	V	DV
Chapman-Enskog-Wilke-Lee Mixture	DV1CEWL	V	DVMX

Thermodynamic Properties Model	Model Name	Phase	Properties
Chung-Lee-Starling low pressure Viscosity	MUL0CLSL, MUL2CLSL	V	MUVLP, MUVMXLP
Chung-Lee-Starling Viscosity	MUV0CLS2, MUV0CLS2	V L	MUV, MUVMX
Chung-Lee-Starling	KV0CLS2, KV2CLS2	V	KV, KVMX
thermal conductivity	KL0CLS2, KL2CLS2	L	KL, KLMX
Dawson-Khoury-Kobayashi Binary	DV1DKK	V	DV
Dawson-Khoury-Kobayashi Mixture	DV1DKK	V	DVMX
Dean-Stiel pressure correction	MUV0DSPC, MUV2DSPC	V	MUVPC, MUVMXPC
Hakim-Steinberg-Stiel / DIPPR	SIG0HSS, SIG2HSS	L	SIGL, SIGLMX
IAPS viscosity	MUV0H2O	V	MUV
	MUL0H2O	L	MUL
IAPS thermal conductivity	KV0H2O	V	KV
	KL0H2O	L	KL
IAPS thermal surface tension	SIG0H2O	L	SIGL
Jones-Dole electrolyte correction	MUL2JONS	L	MULMX
Letsou-Stiel	MUL0LEST, MUL2LEST	L	MUL, MULMX
Lucas	MUV0LUC, MUV2LUC	V	MUV, MUVMX
Nernst-Hartley	DL0NST, DL1nst	L	DL, DLMX
Onsager-Samaras electrolyte correction	SIG2ONSG	L	SIGLMX
Riedel electrolyte correction	KL2RDL	L	KLMX
Sato-Riedel / DIPPR	KL0SR, KL2SRVR	L	KL, KLMX
Stiel-Thodos / DIPPR	KV0STLP	V	KVLP
Stiel-Thodos pressure correction	KV0STPC, KV2STPC	V	KVPC
TRAPP viscosity	MUV0TRAP, MUV2TRAP	V	MUV, MUVMX, MUL, MULMX
	MUL0TRAP, MUL2TRAP	L	
TRAPP thermal conductivity	KV0TRAP, KV2TRAP	V	KV, KVMX
	KL0TRAP, KL2TRAP	L	KL, KLMX
Wassiljewa-Saxena-Maxon mixing rule	KV2WMSM	V	KVMXLP
Wilke-Chang binary	DL0WC2	L	DL
Wilke-Chang mixture	DL1WC	L	DLMX

*Nonconventional Solid
Property Models*

Thermodynamic Properties Model	Model Name	Phase
General Coal Enthalpy Model	HCOALGEN	S
General Density Polynomial	DNSTYGEN	S
General Heat Capacity Polynomial	ENTHGEN	S
IGT Coal Density Model	DCOALIGT	S
IGT Char Density Model	DCHARIGT	S

Property Model Option Codes

The following tables list the model option codes available:

- Option Codes for Transport Property Models
- Option Codes for Activity Coefficient Models
- Option Codes for Equation of State Models
- Option Codes for K-value Models
- Option Codes for Enthalpy Models

*Option Codes for
Transport Property
Models*

Model Name	Option Code	Value	Descriptions
SIG2HSS	1	1	Exponent in mixing rule (default)
		-1,-2,-3	Exponent in mixing rule
SIG2ONSG	1	1	Exponent in mixing rule (default)
		-1,-2,-3	Exponent in mixing rule
MUL2API, MULAPI92	1	0	Release 9 method. First, the API, SG of the mixture is calculated, then the API correlation is used (default)
		1	Pre-release 9 method. Liquid viscosity is calculated for each pseudocomponent using the API method. Then mixture viscosity is calculated by mixing rules.

*Option Codes for Activity
Coefficient Models*

Model Name	Option Code	Value	Descriptions
GMXSH	1	0	No volume term (default)
		1	Includes volume term
WHENRY	1	1	Equal weighting
		2	Size - $VC^{1/3}$
		3	Area - $VC^{2/3}$ (default)
		4	Volume - VC

Model Name	Option Code	Value	Descriptions
GMELC, HAQELC,	1		Defaults for pair parameters
HMXELC, GAQELC,		1	Pair parameters default to zero
GMXELC		2	Solvent/solute pair parameters default to water parameters. Water/solute pair parameters default to zero (default)
		3	Default water parameters to 8, -4. Default solvent/solute parameters to 10, -2
	2		Vapor phase EOS for liquid enthalpy and Gibbs energy
		0	Ideal gas EOS (default)
		1	HF EOS for hydrogen fluoride
	3		Solvent/solvent binary parameter names
		0	Use scalar GMELCA, GMELCB and GMELCM (default)
		1	Use vector NRTL(8)
GMENRTL,	1		Defaults for pair parameters
HMXENRTL,		1	Pair parameters default to zero
GMXENRTL		2	Solvent/solute pair parameters default to water parameters. Water/solute pair parameters default to zero
		3	Default water parameters to 8, -4. Default solvent/solute parameters to 10, -2 (default)
	2		Vapor phase EOS for liquid enthalpy and Gibbs energy
		0	Ideal gas EOS (default)
		1	HF EOS for hydrogen fluoride
	3		Solvent/solvent binary parameter names
		0	Use scalar GMELCA, GMELCB and GMELCM (default)
		1	Use vector NRTL(8)
GMXENRHG,	1		Defaults for pair parameters
GMENRHG,		1	Pair parameters default to zero
HMXENRHG		2	Solvent/solute pair parameters default to water parameters. Water/solute pair parameters default to zero
		3	Default water parameters to 8, -4. Default solvent/solute parameters to 10, -2 (default)
	2		Vapor phase EOS for liquid enthalpy and Gibbs energy
		0	Ideal gas EOS (default)
		1	HF EOS for hydrogen fluoride
	3		Solvent/solvent binary parameter names
		0	Use scalar GMELCA, GMELCB and GMELCM (default)
		1	Use vector NRTL(8)
	4		Standard enthalpy calculation
		0	Standard electrolytes method (Pre release 10)
		1	Helgeson method (default)

Model Name	Option Code	Value	Descriptions
	5		Reaction temperature dependency estimation
		0	Do not calculate
		1	Calculate (default)
GMPT1	1		Defaults for pair mixing rule
		-1	No unsymmetric mixing
		0	Unsymmetric mixing polynomial (default)
		1	Unsymmetric mixing integral
GAQPT3, GMPT3,	1		Defaults for pair mixing rule
HAQPT3		-1	No unsymmetric mixing
		0	Unsymmetric mixing polynomial (default)
		1	Unsymmetric mixing integral
	2		Standard enthalpy calculation
		0	Standard electrolytes method (Pre-release 10)
		1	Helgeson method (Default)
	3		Estimation of K-stoic temperature dependency
		0	Use value at 298.15 K
		1	Helgeson Method (default)
HS0POL1,	1		Reference temperature usage
GS0POL1,		0	Use standard reference temperature (default)
SS0POL1		1	Use liquid reference temperature

*Option Codes for
Equation of State Models*

Model Name	Option Code	Value	Descriptions
ESHOC, ESHOC0, PHV0HOC	1	0	Hayden-O'Connell model. Use chemical theory only if one component has HOCETA=4.5 (default)
		1	Always use the chemical theory regardless of HOCETA values
		2	Never use the chemical theory regardless of HOCETA values
ESPR, ESPR0	1	0	ASPEN Boston/Mathias alpha function (default)
		1	Original literature alpha function
ESPRSTD, ESPRSTD0	1	0	ASPEN Boston/Mathias alpha function
		1	Original literature alpha function (default)
ESRKS, ESRKS0	1	0	ASPEN Boston/Mathias alpha function (default)
		1	Original literature alpha function
		2	Grabowski and Daubert alpha function for H2 above TC $(\alpha = 1.202 \exp(-0.30228 \times \text{Tri}))$
ESRKSTD, ESRKSTD0	1	0	ASPEN Boston/Mathias alpha function

Model Name	Option Code	Value	Descriptions
		1	Original literature alpha function (default)
		2	Grabowski and Daubert alpha function for H2 above TC $(\alpha = 1.202\exp(-0.30228 \times \text{Tri})$)
ESRKSW, ESRKSW0	1	0	ASPEN Boston/Mathias alpha function (default)
		1	Original literature alpha function
		2	Grabowski and Daubert alpha function for H2 above TC $(\alpha = 1.202\exp(-0.30228 \times \text{Tri})$)
ESRKU, ESRKU0	1		Initial temperature for binary parameter estimation
		0	At TREF=25 C (default)
		1	The lower of TB(i) or TB(j)
		2	(TB(i) + TB(j))/2
		> 2	Value entered used as temperature
	2		VLE or LLE UNIFAC
		0	VLE (default)
		1	LLE
	3		Property diagnostic level flag (-1 to 8)
	4		Vapor phase EOS used in generation of TPxy data with UNIFAC
		0	Hayden-O'Connell (default)
		1	Redlich-Kwong
	5		Do/do not estimate binary parameters
		0	Estimate (default)
		1	Set to zero
ESHF, ESHF0	1	0	Equation form for Log(k) expression: $\log(\text{K}) = \text{A} + \text{B}/\text{T} + \text{C} \cdot \ln(\text{T}) + \text{D} \cdot \text{T}$ (default)
		1	$\log(\text{K}) = \text{A} + \text{B}/\text{T} + \text{C} \cdot \text{T} + \text{D}/\text{T}^2 + \text{E} \cdot \log(\text{P})$
ESPRWS, ESPRWS0,	1		Equation form for alpha function
ESPRV1, ESPRV10,		1	Original literature alpha function
ESPRV2, ESPRV20,		2	Mathias-Copeman alpha function
		3	Schwartzentruber-Renon alpha function (default)
ESRKSWS, ESRKSWS0 ,	1		Equation form for alpha function
ESRKSV1, ESRKSV10,		1	Original literature alpha function
ESRKSV2, ESRKSV20,		2	Mathias-Copeman alpha function
		3	Schwartzentruber-Renon alpha function (default)

Model Name	Option Code	Value	Descriptions
ESSTEAM,	1	0	ASME 1967 correlations
ESSTEAM0		1	NBS 1984 equation of state (default)
ESH2O, ESH2O0	1	0	ASME 1967 correlations (default)
		1	NBS 1984 equation of state

Option Codes for K-Value Models

Model Name	Option Code	Value	Descriptions
BK10	1	0	Treat pseudocomponents as paraffins (default)
		1	Treat pseudocomponents as aromatics

Option Codes for Enthalpy Models

Model Name	Option Code	Value	Descriptions
DHL0HREF	1	1	Use Liquid reference state for all components (Default)
		2	Use liquid and gaseous reference states based on the state of each component

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 Properties Property 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 the View button. The View Route dialog box appears.

If you click on a route or model on the tree, a short descriptions of the route or model appears in the Prompt area. 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.

There are two ways to look up the equation corresponding to the method number of a route.

The first method, if you are in the Aspen Physical Property System is to:

1 Close the View Route dialog box.

2 Go to the Property field corresponding to the route.

3 Use Help to get online help on methods corresponding to this property.

4 Locate the formula corresponding to the method number.

The second method is to look up the method in the table labeled Vapor Fugacity Coefficient Methods in the section corresponding to the property for which you trace the route (HLMX). The formula is listed next to the method number.

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 and 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.

Modifying and Creating Property Method

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 Chapter 2. 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 Property 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 From the Data menu, select Properties, then Property Method.
  The Property Methods Object Manager appears.

2 Select the property method and click on Edit.
  The Property Methods form appears.

3 Go to the Routes sheet.

4 In the Route ID field of the property of interest, use List 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, the click on 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 Property 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 Property 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 From the Data menu, select Properties, then Property Methods. The Property Methods Object Manager appears.

2 Select the property method and click on Edit. The Property Methods form appears.

3 Go to the Models sheet.

4 On the Model name field of the property of interest, use List for 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, this chapter. 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 Properties 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 Properties Property Methods Object Manager.

5 Select the new property method, then click Edit.

The second way to begin is:

1 From the Data menu, select Properties, then Property Methods.

The Property Methods Object Manager appears.

2 Click on New and enter the new property method name.

The Property Methods form appears.

Then for both methods do the following steps:

1 Select the Property Methods .Routes or the Property Methods .Models sheet.

2 On the Base property method field, use List and 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

To use a second data set with a model:

1 From the Data menu, select Properties, then Property Methods.

The Property Methods Object Manager appears.

2 Select the property method and click on Edit.

The Property Methods form appears.

3 Go to the Models sheet.

The DataSet 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 Properties 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.

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.

2   From the Data menu, select Properties, then Advanced, then 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 Property Methods Routes sheet which route you want to modify.

3   Click on 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
    - 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 Property 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 Properties Advanced 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 Property 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. Use List from the Model name field to select HL2USR, the liquid mixture enthalpy user model.

Reference the route HLMXAP in the property method on the Property Methods Routes sheet. You can check that the user enthalpy model HL2USR appears on the Property Methods Models sheet.

Electrolyte Calculation

Overview

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
- 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 Reactions 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 Reactions 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:

$$2H_2O \quad \leftrightarrow \quad H_3O^+ + OH^- \tag{2}$$

$$NH_3 + H_2O \quad \leftrightarrow \quad NH_4^+ + OH^- \tag{3}$$

$$H_2S + H_2O \quad \leftrightarrow \quad H_3O^+ + HS^- \tag{4}$$

$$HS^- + H_2O \quad \leftrightarrow \quad H_3O^+ + S^{-2} \tag{5}$$
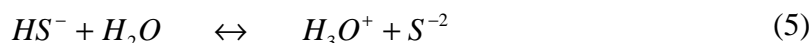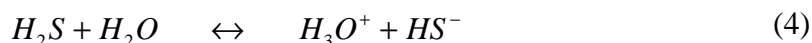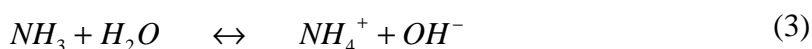
Five ionic species are thereby produced from these aqueous phase ionic reactions. All components in these reactions exist at chemical equilibrium conditions and are the true components of the

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 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.

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 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.

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

Generally, the apparent component approach is preferred for simple electrolyte systems. It offers the advantage that only apparent components need to be comsidered. 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. When the apparent components yield volatile reaction products, always use the true component approach.

If you use the apparent component approach, solution chemistry is required.

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 Chapter 3.

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:

$$n_{ca}^a = \frac{n_c^t n_a^t}{\sum_c z_c n_c^t}$$

(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, $(Ca_2SO_4)_2$ 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:

$$x_k^a = \frac{n_k^a}{n_{tot}^a}$$

(8)

Where k can refer to any solvent B, molecular solute i, or apparent electrolyte ca.

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.

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 Debije-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.

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.

Future Models   Active research is being conducted in the field of electrolyte thermodynamics (Mauer, 1983). For example, models based on Mean Spherical Approximation (Planche and Renon, 1981, Watanasiri et al., 1982) and equation of state electrolyte models (Fürst and Renon, 1993) are being developed. Generally, the trend is toward developing thermodynamically consistent models with fewer adjustable parameters, broader applicability, and greater predictive capability. A broad range of electrolyte activity coefficient models will soon be available.

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 Aspen Plus User Guide, Chapter 31 or Aspen Properties User Guide, for details on data regression.

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Free-Water and Rigorous Three-Phase Calculations

Overview

This chapter describes free-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 and/or rigorous three-phase calculations can be performed.

Unit Operation Models That Allow Three-Phase Calculations

Name	Description	Free-Water Calculations	Water Decant Stream	Rigorous Three-Phase Calculations
Mixer	Stream mixer	YES	YES	YES
FSplit	Stream splitter	YES	NO	YES
Sep	Component separator	YES	NO	YES
Sep2	Two outlet separator	YES	NO	YES
DSTWU	Shortcut distillation design	YES †	YES	NO
Distl	Shortcut distillation rating	YES †	YES	NO
SCFrac	Shortcut petroleum distillation	YES †	YES	NO
RadFrac	Rigorous distillation	YES	YES	YES
MultiFrac	Rigorous multicolumn distillation	YES	YES	NO
PetroFrac	Rigorous petroleum distillation	YES	YES	NO
BATCHFRAC	Rigorous batch distillation	YES †	NO	YES
RATEFRAC	Rate-based distillation	YES †	YES	NO
Extract	Rigorous liquid-liquid extractor	NO	NO	††
Heater	Heater/cooler	YES	YES	YES
Flash2	Two outlet flash	YES	YES	YES
Flash3	Three outlet flash	NO	NO	YES
Decanter	Liquid-liquid decanter	YES	NO	††
Heatx	Two stream heat exchanger	YES	YES	YES
MHeatx	Multistream heat exchanger	YES	YES	YES
RStoic	Stoichiometric reactor	YES	YES	YES
RYield	Yield reactor	YES	YES	YES
RGibbs	Equilibrium reactor Gibbs energy minimization	NO	NO	YES †††
Pump	Pump/hydraulic turbine	YES	YES	YES
Compr	Compressor/turbine	YES	YES	YES
MCompr	Multistage compressor/turbine	YES	YES	YES
Crystallizer	Crystallizer	NO	NO	NO
Pipeline	Pipeline	YES	NO	YES
Dupl	Stream duplicator	—	—	—
Mult	Stream multiplier	—	—	—

† Condenser only

†† Rigorous liquid-liquid equilibrium calculations

††† RGibbs handles any number of phases rigorously.

Free-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, when performing flash calculations or liquid-liquid equilibrium calculations on water-organic systems in which the water phase is essentially pure.

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.

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 rigorous three-phase calculations.

For chemical systems such as water-higher alcohols, free-water calculations do not apply. Solubility of the organics in the water phase is significant. Rigorous three-phase calculations are required.

Specifying Free-Water Calculations

The free-water calculations are completely rigorous, except for the assumption that the water phase is pure. If free 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 calculations for	Use the Free-Water field on the
The entire flowsheet	Setup Specifications Global sheet
An individual unit operation block	Blockops 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.

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 the Aspen Plus User Guide, Chapter 10.

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 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 Properties Specifications Global sheet or the Blockops form.

Solu-water option	Calculate γ_w from	Calculate φ_w^v from
0	$\gamma_w = \dfrac{1}{x_w^{sol}}$	Free-water property method
1	$\gamma_w = \dfrac{1}{x_w^{sol}}$	Primary property method
2	$\gamma_w = f(T, x_w)$ where $\gamma_w = \dfrac{1}{x_w^{sol}}$ when $x_w = x_w^{sol}$	Primary property method
3	Primary property method	Primary property method

Solu-water option 3 is not recommended unless binary interaction parameters regressed from liquid-liquid equilibrium data are available.

The limiting solubility of water in the organic phase $\left(x_w^{sol}\right)$ 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 ith organic species
x_{wi}^{sol}	=	Mole fraction solubility of water in the ith species

The value of x_{wi}^{sol} is calculated as a function of temperature, using the Water Solubility model (WATSOL).

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.

Petroleum Components Characterization Methods

Overview

The Aspen Physical Property System provides a wide range of methods for characterization of petroleum components, or pseudocomponents. These methods are used to estimate property parameters, such as critical properties, ideal gas heat capacity, vapor pressure, and liquid viscosity. The following table lists the:

- Parameters that the Aspen Physical Property System estimates for petroleum components

- Methods available. The literature references for each method are listed at the end of this chapter.

Petroleum Components Characterization Methods

Parameter	Description	Model Available
MW	Molecular weight	Brule et al. (1982) Hariu-Sage (1969) Hariu-Sage-Aspen (1994) Kesler-Lee (1976) Riazi API (1987) Riazi-Daubert (1980) Tsang-Aspen (1978)
TC	Critical temperature	Brule et al. (1982) Cavett (1962) Kesler-Lee (1976) Riazi API (1987) Riazi-Daubert (1980) Tsang-Aspen (1978) Twu (1984)

Parameter	Description	Model Available
PC	Critical pressure	Cavett (1962) Kesler-Lee (1976) Riazi API (1987) Riazi-Daubert (1980) Tsang-Aspen (1978) Twu (1984)
VC	Critical volume	Brule et al. (1982) Reidel (1954) Twu (1984)
PL	Vapor pressure	BK-10 Kesler-Lee (1980) Maxwell-Bonnell (1955) Tsang-SWAP (1978)
CPIG	Ideal gas heat capacity	Brule et al. (1982) Cavett (1962) Kesler-Lee (1976) Mathias-Monks (1982) Tsang-Aspen (1978)
VL	Liquid molar volume	Cavett Rackett (Spencer, 1972)
DHVL	Enthalpy of vaporization	Vetere (1973)
OMEGA	Acentric factor	Defining relation Kesler-Lee (1976) Kesler-Lee-Aspen (1994)
MUL	Liquid viscosity	Watson (1935)
BWRGMA	BWR orientation parameter	Brule et al. (1982)
TCBWR	BWR critical temperature	Brule et al. (1982)
VCBWR	BWR critical volume	Brule et al. (1982)
DHFORM	Standard enthalpy of formation	Default to zero Montgomery (1988)
DGFORM	Standard Gibbs energy of formation	Default to zero Montgomery (1988)
WATSOL	Water solubility in hydrocarbon	Aspen Physical Property System API Kerosene Hibbard-Schalla
RKSKIJ	RKS binary parameters	API 1978 API 1987

Property Methods for Characterization of Petroleum Components

Since there are several methods available for estimation of a given parameter, the Aspen Physical Property System selects the most appropriate method for a given application. These selected methods are used to create an property method. There are five property methods 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.

The property methods available for characterization of pseudocomponents are listed in the following table.

Property Methods for Pseudocomponents Characterization

Property Method ASPEN: Aspen Tech and API procedures

Property	Method
Molecular weight	Hariu-Sage-ASPEN
Tc	Riazi-Daubert
Pc	Riazi-Daubert
Vc	Reidel
Vapor pressure	BK-10
Ideal gas capacity	Kesler-Lee
Liquid molar volume	Rackett
Enthalpy of vaporization	Vetere
Acentric factor	Kesler-Lee-ASPEN
Viscosity	Watson
Water solubility	Aspen Physical Property System
Standard enthalpy of formation	Montgomery
Standard Gibbs energy of formation	Montgomery
RKS binary parameters	API 1978

Property Method API-METH: API Procedures

Property	Method
Molecular weight	Hariu-Sage
Tc	Riazi-Daubert
Pc	Riazi-Daubert
Vc	Reidel
Vapor pressure	Maxwell-Bonnell
Ideal gas heat capacity	Kesler-Lee
Liquid molar volume	Rackett
Enthalpy of vaporization	Vetere
Acentric factor	Kesler-Lee
Viscosity	Watson
Water Solubility	Aspen Physical Property System
Standard enthalpy of formation	Default to zero
Standard Gibbs energy of formation	Default to zero
Water solubility in hydrocarbon	Aspen Physical Property System
RKS binary parameters	API 1978

Property Method API-METH: For COAL-LIQ; for Coal Liquids

Property	Method
Molecular weight	Hariu-Sage
Tc	Tsang-ASPEN
Pc	Tsang-ASPEN
Vc	Reidel
Vapor pressure	Tsang-SWAP
Ideal gas heat capacity	Mathias-Monks
Liquid molar volume	Rackett
Enthalpy of vaporization	Vetere
Acentric factor	Kesler-Lee
Viscosity	Watson
BWR orientation parameter	Brule et al.
BWR Tc	Brule et al.
BWR Vc	Brule et al.
Standard enthalpy of formation	Default to zero
Standard Gibbs energy of formation	Default to zero
RKS binary parameters	API 1978

Property Method LK: Lee-Kesler

Property	Method
Molecular weight	Kesler-Lee
Tc	Kesler-Lee
Pc	Kesler-Lee
Vc	Reidel
Vapor pressure	Kesler-Lee
Ideal gas heat capacity	Kesler-Lee
Liquid molar volume	Rackett
Enthalpy of vaporization	Vetere
Acentric factor	Kesler-Lee
Viscosity	Watson
Standard enthalpy of formation	Aspen Physical Property System
Standard Gibbs energy of formation	Montgomery
Water solubility in hydrocarbon	Montgomery
RKS binary parameters	API 1978

Property Method API-TWU: AspenTech, API, and Twu

Property	Method
Molecular weight	Hariu-Sage-ASPEN
Tc	Twu
Pc	Twu
Vc	Twu
Vapor pressure	BK-10
Ideal gas heat capacity	Kesler-Lee
Liquid molar volume	Rackett
Enthalpy of vaporization	Vetere
Acentric factor	Kesler-ASPEN
Viscosity	Watson
Water solubility	API kerosene-line
Standard enthalpy of formation	Montgomery
Standard Gibbs energy of formation	Montgomery
RKS binary parameters	API 1978

Water Solubility in Petroleum Pseudocomponents

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

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.

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Property Parameter Estimation

Overview

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

Pure Component Constants

Parameter	Description	Model †
MW	Molecular weight	
TB	Normal boiling point	
TC	Critical temperature	
PC	Critical pressure	
VC	Critical volume	
ZC	Critical compressibility factor	
DHFORM	Standard heat of formation at $25°\,C$	
DGFORM	Standard Gibbs free energy of formation at $25°\,C$	
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 $25°$ C	
GMUQR	UNIQUAC R parameter	UNIQUAC
GMUQQ	UNIQUAC Q parameter	UNIQUAC
PARC	Parachor ††	
DHSFRM	Solid enthalpy of formation at $25°$ C	
DGSFRM	Solid Gibbs energy of formation at $25°$ C	
DHAQHG	Aqueous infinite dilution enthalpy of formation	Helgeson
DGAQHG	Aqueous infinite dilution Gibbs energy of formation	Helgeson
S25HG	Entropy at $25°$ C	Helgeson

Temperature-Dependent Property Correlation Parameters

Parameter	Description	Model †
CPIG	Ideal gas heat capacity	Ideal Gas Heat Capacity/DIPPR
CPLDIP	Liquid heat capacity	Liquid Heat Capacity, DIPPR
CPSPO1	Solid heat capacity	Solid Heat Capacity
PLXANT	Vapor pressure	Antoine/Wagner
DHVLWT	Heat of vaporization	Watson/DIPPR
RKTZRA	Liquid molar volume	Rackett/DIPPR
OMEGHG	Helgeson OMEGA heat capacity coefficient	Helgeson
CHGPAR	Helgeson C Heat Capacity Coefficient	Helgeson
MUVDIP	Vapor viscosity	Chapman-Enskog-Brokaw/DIPPR
MULAND	Liquid viscosity	Andrade/DIPPR
KVDIP	Vapor thermal conductivity	Stiel-Thodos/DIPPR
KLDIP	Liquid thermal conductivity	Sato-Riedel/DIPPR
SIGDIP	Surface tension	Hakim-Steinberg-Stiel/DIPPR

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

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

† See Chapter 3 for more information on models.

†† Parachor is needed in estimating surface tension and radius of gyration

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.

Molecular Weight (MW)   If you use the general method to enter molecular structure on the Properties 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 Properties 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 Properties 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	TC, PC, Vapor pressure data

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 equation when one or two experimental vapor pressure data are available. This method can also be used to estimate TC 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.

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 one or two experimental vapor pressure values are available. 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.

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:

$$Z_c = \frac{P_c V_c}{RT_c}$$

Where:

R	=	Universal gas constant
P_c	=	Critical pressure
V_c	=	Critical volume
T_c	=	Critical temperature

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_{ci}) 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).

Standard Enthalpy of Formation (DHFORM)

PCES provides the following methods for estimating standard enthalpy of formation:

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.

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.

Standard Gibbs Free Energy of Formation (DGFORM)

PCES provides the following methods for estimating standard Gibbs free energy of formation:

Method	Information Required
Joback	Structure
Benson	Structure
Gani	Structure

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
Heat of Vaporization at TB (DHVLB)	PCES estimates heat of vaporization at the normal boiling point by applying the heat of vaporization correlation (DHVLWT) at TB.
Liquid Molar Volume at TB (VB)	PCES estimates liquid molar volume at the normal boiling point by applying the Rackett equation (RKTZRA) at TB.
Standard Liquid Volume (VLSTD)	PCES estimates standard liquid volume by applying the Rackett liquid molar volume correlation (RKTZRA) 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* 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.*
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 Ideal-Gas-Heat-Capacity-Polynomial 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 Properties Data Pure Component form.

Vapor Pressure (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	TC, PC, (vapor pressure data)

The Extended Antoine 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 Properties 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 vapor pressure data values are available. 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.

Heat of Vaporization (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 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 Properties 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 (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 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 Properties Data Pure Component form.

Liquid Viscosity (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 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 Properties Data Pure Component form.

Vapor Viscosity (MUVDIP)

PCES provides the following methods for estimating vapor viscosity:

Method	Information Required
Data	Vapor viscosity data
Reichenberg	Structure, MW,TC, PC

The DIPPR 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 DIPPR vapor viscosity correlation parameters by fitting experimental vapor viscosity data you enter on the Properties Data Pure Component form.

Liquid Thermal Conductivity (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 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 Properties Data Pure Component form.

Vapor Thermal Conductivity (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. Use the Properties Data Pure Component form to enter experimental vapor thermal conductivity data.

Surface Tension (SIGDIP)

PCES provides the following methods for estimating surface tension:

Method	Information Required
Data	Surface tension data
Brock-Bird	TB, TC, PC
Macleod-Sugden	TB, TC, PC, VL, PARC
Li-Ma	Structure, TB

The DIPPR 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 Properties 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.

Liquid Heat Capacity (CPLDIP)

PCES provides the following methods for estimating liquid heat capacity:

Method	Information Required
Data	Liquid heat capacity data
Ruzicka	Structure

The DIPPR 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 Properties 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 (CPSPO1)

PCES provides the following methods for estimating solid heat capacity:

Method	Information Required
Data	Solid heat capacity data
Mostafa	Structure

The 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 Properties 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.

Solid Standard Enthalpy of Formation (DHSFRM)

Only the Mostafa method is available for estimating solid standard enthalpy of formation.

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.

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

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:

$$DHAQHG = DGAQFM + 298.15 * (S025C - S025E)$$

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:

$$DHAQHG = 1.105 * DGAQFM - 12822.8$$

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:

$$DHAQHG = 122111.3214 + 3137.4034 * (S025C - S025E)$$

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
AQU-EST1	DHAQFM
AQU-EST2	S025C

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:

$$DGAQHG = DHAQFM - 298.15 * (S025C - S025E)$$

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:

$$DGAQHG = 122110.2752 + 2839.2534 * (S025C - S025E)$$

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:

$$S25HG = \frac{(DHAQFM - DGAQFM)}{298.15} + S025E$$

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:

$$S25HG = 3.52205x10^{-4} * DGAQFM - 43.00788 + S025E$$

where $S025E$ is the sum of absolute entropy of the constituent elements of a compound at $25°$ C.

AQU-EST2 Method

If DHAQFM is in the databank, the AQU-EST2 method estimates absolute entropy using an empirical relation developed by Aspen Technology, as follows:

$$S25HG = 3.187349x10^{-4} * DHAQFM - 38.9208 + S025E$$

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.

Binary Parameters (WILSON, NRTL, UNIQ)

PCES estimates binary parameters for the WILSON, NRTL, and UNIQUAC models, using infinite-dilution activity coefficients. Infinite-dilution activity coefficients can be supplied by:

• Laboratory data entered on the Properties Data Mixture form, with data type=GAMINF

• Estimation, using the UNIFAC, UNIF-LL, UNIF-DMD or UNIF-LBY method

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) 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.

UNIFAC R and Q Parameters (GMUFR, GMUFQ, GMUFDR, GMUFDQ, GMUFLR, GMUFLQ)

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. Table 3.3 in *Physical Property Data* lists the functional groups for the Bondi method.

Bromley-Pitzer Activity Coefficient Model

Overview

The Bromley-Pitzer activity coefficient model is a simplified Pitzer model with the interaction parameters estimated with the Bromley's method. It can be used to compute activity coefficients for aqueous electrolytes up to 6 molal ionic strength. This model is less accurate than the Pitzer model. The model should not be used for mixed-solvent electrolyte systems

Working Equations

The complete Pitzer equation (Fürst and Renon, 1982) for the excess Gibbs energy is (see also Appendix C, equation 4):

$$\frac{G^E}{RT} = n_W\left[f(I) + \sum_i \sum_j B_{ij} m_i m_j + \sum_i \sum_j \theta_{ij} m_i m_j + \frac{1}{2}\sum_i \sum_j \left(\sum_k m_k z_k\right) C_{ij} m_i m_j + \frac{1}{6}\sum_i \sum_j \sum_k \psi_{ijk} m_i m_j m_k \right] \quad (1)$$

Where:

G^E	=	Excess Gibbs energy
R	=	Gas constant
T	=	Temperature
n_w	=	Kilograms of water
z_i	=	Charge number of ion i
$m_i = \dfrac{x_i}{x_w}\left(\dfrac{M_w}{1000}\right) = \dfrac{n_i}{n_w}$	=	molality of ion i

Where:

x_i	=	Mole fraction of ion i
x_w	=	Mole fraction of water
M_w	=	Molecular weight of water (g/mol)
n_i	=	Moles of ion i

B, C, θ and Ψ are interaction parameters, and $f(I)$ is an electrostatic term as a function of ionic strength; these terms are discussed in Appendix C. See Appendix C for a detailed discussion of the Pitzer model.

The C term and the Ψ term are dropped from equation 1 to give the simplified Pitzer equation.

$$\frac{G^E}{RT} = n_W \left[f(I) + \sum_i \sum_j B_{ij} m_i m_j + \sum_i \sum_j \theta_{ij} m_i m_j \right] \tag{2}$$

Where:

B_{ij}	=	$f\left(\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}, \beta_{ij}^{(3)}\right)$

Therefore, the simplified Pitzer equation has two types of binary interaction parameters, β's and θ's. There are no ternary interaction parameters with the simplified Pitzer equation.

Note that the Pitzer model parameter databank described in *Physical Property Data*, Chapter 1, is not applicable to the simplified Pitzer equation.

A built-in empirical correlation estimates the $\beta^{(0)}$ and $\beta^{(1)}$ parameters for cation-anion pairs from the Bromley ionic parameters, β_{ion} and δ_{ion} (Bromley, 1973). The estimated values of $\beta^{(0)}$'s and $\beta^{(1)}$'s are overridden by the user's input. For parameter naming and requirements, see Bromley-Pitzer Activity Coefficient Model.

L.A. Bromley, "Thermodynamic Properties of Strong Electrolytes in Aqueous Solution, " *AIChE J.*, Vol. 19, No. 2, (1973), pp. 313 – 320.

Fürst and H. Renon, "Effect of the Various Parameters in the Application of Pitzer's Model to Solid-Liquid Equilibrium Preliminary Study for Strong 1-1 Electrolytes, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 21, No. 3, (1982), pp. 396 – 400.

Parameter Conversion

For 2-2 electrolytes, the parameter $\beta^{(3)}$ corresponds to Pitzer's $\beta^{(1)}$; $\beta^{(2)}$ is the same in both Aspen Physical Property System and original Pitzer models. Pitzer refers to the 2-2 electrolyte parameters as $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(0)}$, $\beta^{(0)}$ and $\beta^{(2)}$ retain their meanings in both models, but Pitzer's $\beta^{(1)}$ is Aspen Physical Property System $\beta^{(3)}$ Be careful to make this distinction when entering 2-2 electrolyte parameters.

Electrolyte NRTL Activity Coefficient Model

Overview

The Electrolyte Non-Random Two Liquid (NRTL) model is a versatile model for the calculation of activity coefficients. Using binary and pair parameters, the model can represent aqueous electrolyte systems as well as mixed solvent electrolyte systems over the entire range of electrolyte concentrations. This model can calculate activity coeffients for ionic species and molecular species in aqueous electrolyte systems as well as in mixed solvent electrolyte systems. The model reduces to the well-known NRTL model when electrolyte concentrations become zero (Renon and Prausnitz, 1969).

The electrolyte NTRL model uses the infinite dilution aqueous solution as the reference state for ions. It adopts the Born equation to account for the transformation of the reference state of ions from the infinite dilution mixed solvent solution to the infinite dilution aqueous solution.

Water must be present in the electrolyte system in order to compute the transformation of the reference state of ions. Thus, it is necessary to introduce a trace amount of water to use the model for nonaqueous electrolyte systems.

Theoretical Basis and Working Equations

In this appendix, the theoretical basis of the model is explained and the working equations are given. The different ways parameters can be obtained are discussed with references to the databank directories and the Data Regression System (DRS). The parameter requirements of the model are given in Electrolyte NRTL Activity Coefficient Model.

Development of the Model

The Electrolyte NRTL model was originally proposed by Chen et al., for aqueous electrolyte systems. It was later extended to mixed solvent electrolyte systems (Mock et al., 1984, 1986). The model is based on two fundamental assumptions:

- *The like-ion repulsion assumption*: states that the local composition of cations around cations is zero (and likewise for anions around anions). This is based on the assumption that the repulsive forces between ions of like charge are extremely large. This assumption may be justified on the basis that repulsive forces between ions of the same sign are very strong for neighboring species. For example, in salt crystal lattices the immediate neighbors of any central ion are always ions of opposite charge.

- *The local electroneutrality assumption*: states that the distribution of cations and anions around a central molecular species is such that the net local ionic charge is zero. Local electroneutrality has been observed for interstitial molecules in salt crystals.

Chen proposed an excess Gibbs energy expression which contains two contributions: one contribution for the long-range ion-ion interactions that exist beyond the immediate neighborhood of a central ionic species, and the other related to the local interactions that exist at the immediate neighborhood of any central species.

The unsymmetric Pitzer-Debije-Hückel model and the Born equation are used to represent the contribution of the long-range ion-ion interactions, and the Non-Random Two Liquid (NRTL) theory is used to represent the local interactions. The local interaction contribution model is developed as a symmetric model, based on reference states of pure solvent and pure completely dissociated liquid electrolyte. The model is then normalized by infinite dilution activity coefficients in order to obtain an unsymmetric model. This NRTL expression for the local interactions, the Pitzer-Debije-Hückel expression, and the Born

equation are added to give equation 1 for the excess Gibbs energy (see the following note).

$$\frac{G_m^{*E}}{RT} = \frac{G_m^{*E,PDH}}{RT} + \frac{G_m^{*E,Born}}{RT} + \frac{G_m^{*E,lc}}{RT} \tag{1}$$

This leads to

$$\ln \gamma_i^* = \ln \gamma_i^{*PDH} + \ln \gamma_i^{*Born} + \ln \gamma_i^{*lc} \tag{2}$$

Note: The notation using * to denote an unsymmetric reference state is well-accepted in electrolyte thermodynamics and will be maintained here. The reader should be warned not to confuse it with the meaning of * in classical thermodynamics according to IUPAC/ISO, referring to a pure component property. In fact in the context of G or γ, the asterisk as superscript is never used to denote pure component property, so the risk of confusion is minimal. For details on notation, see Chapter 1.

Long-Range Interaction Contribution

The Pitzer-Debije-Hückel formula, normalized to mole fractions of unity for solvent and zero for electrolytes, is used to represent the long-range interaction contribution.

$$\frac{G_m^{*E,PDH}}{RT} = -\left(\sum_k x_k\right)\left(\frac{1000}{M_B}\right)^{1/2}\left(\frac{4A_\varphi I_x}{\rho}\right)\ln\left(1 + \rho I_x^{1/2}\right) \tag{3}$$

Where:

x_k	=	Mole fraction of component k
M_B	=	Molecular weight of the solvent B
A_φ	=	Debije-Hückel parameter:
A_φ	=	$\frac{1}{3}\left(\frac{2\pi N_A d}{1000}\right)^{1/2}\left(\frac{Q_e^2}{\varepsilon_w kT}\right)^{3/2}$ (4)
N_A	=	Avogadro's number
d	=	Density of solvent
Q_e	=	Electron charge
ε_w	=	Dielectric constant of water
T	=	Temperature
k	=	Boltzmann constant
I_x	=	Ionic strength (mole fraction scale):

$$I_x \qquad = \qquad \tfrac{1}{2}\sum_i x_i z_i^2 \qquad\qquad (5)$$

$x_i \qquad = \qquad$ Mole fraction of component i

$z_i \qquad = \qquad$ Charge number of ion i

$\rho \qquad = \qquad$ "Closest approach" parameter

Taking the appropriate derivative of equation 3, an expression for the activity coefficient can then be derived.

$$\ln \gamma_i^{*PDH} = -\left(\frac{1000}{M_B}\right)^{\!\frac{1}{2}} A_\varphi\left[\left(\frac{2z_i^2}{\rho}\right)\ln\!\left(1+\rho I_x^{\frac{1}{2}}\right) + \frac{z_i^2 I_x^{\frac{1}{2}} - 2I_x^{\frac{3}{2}}}{1+\rho I_x^{\frac{1}{2}}}\right] \qquad (6)$$

The Born equation is used to account for the Gibbs energy of transfer of ionic species from the infinite dilution state in a mixed-solvent to the infinite dilution state in aqueous phase.

$$\frac{G_m^{*E,Born}}{RT} = \frac{Q_e^2}{2kT}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_w}\right)\left(\frac{\sum_i x_i z_i^2}{r_i}\right)10^{-2} \qquad (7)$$

Where:

$r_i \qquad = \qquad$ Born radius

The expression for the activity coefficient can be derived from (7):

$$\ln \gamma_i^{*Born} = \frac{Q_e^2}{2kT}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_w}\right)\frac{z_i^2}{r_i}10^{-2} \qquad (8)$$

Local Interaction Contribution

The local interaction contribution is accounted for by the Non-Random Two Liquid theory. The basic assumption of the NRTL model is that the nonideal entropy of mixing is negligible compared to the heat of mixing: this is indeed the case for electrolyte systems. This model was adopted because of its algebraic simplicity and its applicability to mixtures that exhibit liquid phase splitting. The model does not require specific volume or area data.

The effective local mole fractions X_{ji} and X_{ii} of species j and i, respectively, in the neighborhood of i are related by:

$$\frac{X_{ji}}{X_{ii}} = \left(\frac{X_j}{X_i}\right)G_{ji} \qquad (9)$$

Where:

$$X_j \qquad = \qquad x_j C_j \quad C_j = z_j \text{ for ions and } C_j = \text{ unity for molecules)}$$

$$G_{ji} \qquad = \qquad e^{\left(-\alpha_{ji}\tau_{ji}\right)}$$

$$\tau_{ji} \qquad = \qquad \frac{g_{ji} - g_{ii}}{RT}$$

$$\alpha_{ji} \qquad = \qquad \text{Nonrandomness factor}$$

g_{ji} and g_{ii} are energies of interaction between species j and i, and i and i, respectively. Both g_{ij} and α_{ij} are inherently symmetric ($g_{ji} = g_{ij}$ and $\alpha_{ji} = \alpha_{ij}$).

Similarly,

$$\frac{X_{ji}}{X_{ki}} = \left(\frac{X_j}{X_k}\right) G_{ji,ki} \tag{10}$$

Where:

$$G_{ji,ki} \qquad = \qquad e^{\left(-\alpha_{ji,ki}\tau_{ji,ki}\right)}$$

$$\tau_{ji,ki} \qquad = \qquad \frac{g_{ji} - g_{ki}}{RT}$$

$$\alpha_{ji,ki} \qquad = \qquad \text{Nonrandomness factor}$$

Apparent Binary Systems

The derivations that follow are based on a simple system of one completely dissociated liquid electrolyte *ca* and one solvent *B*. They will be later extended to multicomponent systems. In this simple system, three different arrangements exist:

**solvent at
center**   **cation at
center**   **anion at
center**
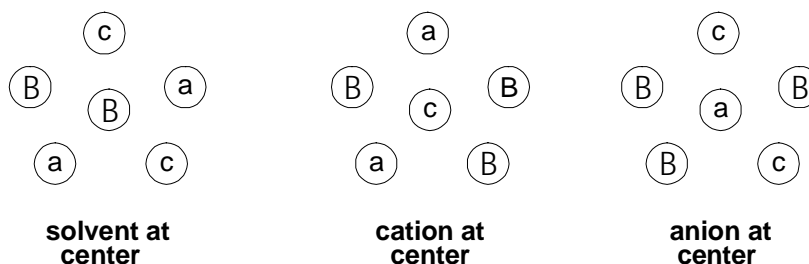
In the case of a central solvent molecule with other solvent molecules, cations, and anions in its immediate neighborhood, the principle of local electroneutrality is followed: the surrounding cations and anions are such that the neighborhood of the solvent is electrically neutral. In the case of a central cation (anion) with solvent molecules and anions (cations) in its immediate

neighborhood, the principle of like-ion repulsion is followed: no ions of like charge exist anywhere near each other, whereas opposite charged ions are very close to each other.

The effective local mole fractions are related by the following expressions:

$$X_{cB} + X_{aB} + X_{BB} = 1 \text{ (central solvent cells)} \tag{11}$$

$$X_{Bc} + X_{ac} = 1 \text{ (central cation cells)} \tag{12}$$

$$X_{Ba} + X_{ca} = 1 \text{ (central anion cells)} \tag{13}$$

Using equation 11 through 13 and the notation introduced in equations 9 and 10 above, expressions for the effective local mole fractions in terms of the overall mole fractions can be derived.

$$X_{iB} = \frac{X_i G_{iB}}{X_a G_{cB} + X_c G_{cB} + X_B G_{BB}} \quad i = c, a, \text{ or } B \tag{14}$$

$$X_{ac} = \frac{X_a}{X_a + X_B G_{Bc,ac}} \tag{15}$$

$$X_{ca} = \frac{X_c}{X_c + X_B G_{Ba,ca}} \tag{16}$$

To obtain an expression for the excess Gibbs energy, let the residual Gibbs energies, per mole of cells of central cation, anion, or solvent, respectively, be $G_m(c-cell)$, $G_m(a-cell)$, and $G_m(B-cell)$. These are then related to the effective local mole fractions:

$$G_m(c-cell) = z_c\left(X_{Bc} g_{Bc} + X_{ac} g_{ac}\right) \tag{17}$$

$$G_m(a-cell) = z_a\left(X_{Ba} g_{Ba} + X_{ca} g_{ca}\right) \tag{18}$$

$$G_m(B-cell) = X_{aB} g_{aB} + X_{cB} g_{cB} + X_{BB} g_{BB} \tag{19}$$

The reference Gibbs energy is determined for the reference states of completely dissociated liquid electrolyte and of pure solvent. The reference Gibbs energies per mole are then:

$$G_m(c-cell) = z_c g_{ac} \tag{20}$$

$$G_m(a-cell) = z_a g_{ca} \tag{21}$$

$$G_m(B-cell) = g_{BB} \tag{22}$$

Where:

z_c =   Charge number on cations

$$z_a \qquad = \qquad \text{Charge number on anions}$$

The molar excess Gibbs energy can be found by summing all changes in residual Gibbs energy per mole that result when the electrolyte and solvent in their reference state are mixed to form the existing electrolyte system. The expression is:

$$G_m^{E,lc} = x_m\left(G_m(B-cell) - G_m^{ref}(B-cell)\right) + x_c\left(G_m(c-cell) - G_m^{ref}(c-cell)\right) \quad (23)$$
$$+ x_a\left(G_m(a-cell) - G_m^{ref}(a-cell)\right)$$

Using the previous relation for the excess Gibbs energy and the expressions for the residual and reference Gibbs energy (equations 17 to 19 and 20 to 22), the following expression for the excess Gibbs energy is obtained:

$$\frac{G_m^{E,lc}}{RT} = X_B X_{cB} \tau_{cB} + X_B X_{aB} \tau_{aB} + X_c X_{Bc} z_c \tau_{Bc,ac} + X_a X_{Ba} z_a \tau_{Ba,ca} \qquad (24)$$

The assumption of local electroneutrality applied to cells with central solvent molecules may be stated as:

$$X_{aB} = X_{cB} \qquad (25)$$

Combining this expression with the expression for the effective local mole fractions given in equations 9 and 10, the following equality is obtained:

$$G_{aB} = G_{cB} \qquad (26)$$

The following relationships are further assumed for nonrandomness factors:

$$\alpha_{aB} = \alpha_{cB} = \alpha_{ca,B} \qquad (27)$$

$$\alpha_{Bc,ac} = \alpha_{Ba,ca} = \alpha_{B,ca} \qquad (28)$$

and,

$$\alpha_{ca,B} = \alpha_{B,ca} \qquad (29)$$

It can be inferred from equations 9, 10, and 26 to 29 that:

$$\tau_{aB} = \tau_{cB} = \tau_{ca,B} \qquad (30)$$

$$\tau_{Bc,ac} = \tau_{Ba,ca} = \tau_{B,ca} \qquad (31)$$

The binary parameters, $\alpha_{ca,B}$, $\tau_{ca,B}$ and $\tau_{B,ca}$ are now the adjustable parameters for an apparent binary system of a single electrolyte and a single solvent.

The excess Gibbs energy expression (equation 24) must now be normalized to the infinite dilution reference state for ions:

$$\frac{G_m^{*E,lc}}{RT} = \frac{G_m^{E,lc}}{RT} - x_c \ln \gamma_c^\infty - x_a \ln \gamma_a^\infty \tag{32}$$

This leads to:

$$\frac{G_m^{*E,lc}}{RT} = X_B \left(X_{cB} + X_{aB} \right) \tau_{ca,B} + X_c X_{Bc} \tau_{B,ca} + X_a X_{Ba} \tau_{B,ca}$$
$$- X_c \left(\tau_{B,ca} + G_c \tau_{ca,B} \right) - X_a \left(\tau_{B,ca} + G_{aB} \tau_{ca,B} \right) \tag{33}$$

By taking the appropriate derivatives of equation 33, expressions for the activity coefficients of all three species can be determined.

$$\frac{1}{z_c} \ln \gamma_c^{*lc} = \frac{X_B^2 \tau_{cB} G_{cB}}{\left(X_c G_{cB} + X_a G_{aB} + X_B \right)^2} + \frac{X_a \tau_{Ba} X_B G_{Ba}}{\left(X_c + X_B G_{Ba} \right)^2} \tag{34}$$
$$+ \frac{X_B \tau_{Bc} G_{Bc}}{\left(X_a + X_B G_{Bc} \right)} - \tau_{Bc} - G_{cB} \tau_{cB}$$

$$\frac{1}{z_a} \ln \gamma_a^{*lc} = \frac{X_B^2 \tau_{aB} G_{aB}}{\left(X_c G_{cB} + X_a G_{aB} + X_B \right)^2} + \frac{X_c \tau_{Bc} X_B G_{Bc}}{\left(X_a + X_B G_{Bc} \right)^2} \tag{35}$$
$$+ \frac{X_B \tau_{Ba} G_{Ba}}{\left(X_c + X_B G_{Ba} \right)} - \tau_{Ba} - G_{aB} \tau_{aB}$$

$$\ln \gamma_B^{lc} = X_{cB} \tau_{cB} + X_{aB} \tau_{aB} + \frac{X_c G_{Bc} \tau_B X_a}{\left(X_a + G_{Bc} X_B \right)^2} + \frac{X_a G_{Ba} \tau_{Ba} X_c}{\left(X_c + G_{Ba} X_B \right)^2} \tag{36}$$
$$- \frac{X_c X_B G_{cB} \tau_{cB}}{\left(X_c G_{cB} + X_a G_{aB} + X_B \right)^2} - \frac{X_a X_B G_{aB} \tau_{aB}}{\left(X_c G_{cB} + X_a G_{aB} + X_B \right)^2}$$

Multicomponent Systems

The Electrolyte NRTL model can be extended to handle multicomponent systems.

The excess Gibbs energy expression is:

$$\frac{G_m^{E,lc}}{RT} = \sum_B X_B \frac{\sum_j X_j G_{jB} \tau_{jB}}{\sum_k X_k G_{kB}} + \sum_c X_c \sum_{a'} \left(\frac{X_a}{\sum_{a''} X_{a''}} \right) \frac{\sum_j X_j G_{jc,a'c} \tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}} \tag{37}$$
$$+ \sum_a X_a \sum_{c'} \left(\frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{\sum_j X_j G_{ja,c'a} \tau_{ja,c'a}}{\sum_k X_k G_{ka,c'a}}$$

Where:

j and k can be any species (a, C, or B)

The activity coefficient equation for molecular components is given by:

$$\ln \gamma_B^{lc} = \frac{\sum_j X_j G_{jB} \tau_{jB}}{\sum_k X_k G_{kB}} + \sum_{B'} \frac{X_{B'} G_{BB'}}{\sum_k X_k G_{kB'}} \left(\tau_{BB'} - \frac{\sum_k X_k G_{kB'} \tau_{kB'}}{\sum_k X_k G_{kB'}} \right) \tag{38}$$

$$+ \sum_c \sum_{a'} \frac{X_a}{\sum_{a''} X_{a''}} \frac{X_c G_{Bc,a'c}}{\sum_k X_k G_{kc,a'c}} \left(\tau_{Bc,a'c} - \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right)$$

$$+ \sum_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{X_a G_{Ba,c'a}}{\sum_k X_k G_{ka,c'a}} \left(\tau_{Bc,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right)$$

The activity coefficient equation for cations is given by:

$$\frac{1}{z_c} \ln \gamma_c^{lc} = \sum_{a'} \left(\frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} + \sum_{B'} \frac{X_B G_{cB}}{\sum_k X_k G_{kB}} \left(\tau_{cB} - \frac{\sum_k X_k G_{kB} \tau_{kB}}{\sum_k X_k G_{kB}} \right) \tag{39}$$

$$+ \sum_a \sum_{c'} \left(\frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{X_a G_{ca,c'a}}{\sum_k X_k G_{ka,c'a}} \left(\tau_{ca,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right)$$

The activity coefficient equation for anions is given by:

$$\frac{1}{z_a} \ln \gamma_a^{lc} = \sum_{c'} \left(\frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} + \sum_B \frac{X_{Bm} G_{aB}}{\sum_k X_k G_{kB}} \left(\tau_{aB} - \frac{\sum_k X_k G_{kB} \tau_{kB}}{\sum_k X_k G_{kB}} \right) \tag{40}$$

$$+ \sum_c \sum_{a'} \left(\frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{X_c G_{ac,a'c}}{\sum_k X_k G_{kc,a'c}} \left(\tau_{ac,a'c} - \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right)$$

Where:

$$G_{cB} = \frac{\sum_a X_a G_{ca,B}}{\sum_{a'} X_{a'}} \tag{41}$$

$$G_{aB} = \frac{\sum_c X_c G_{ca,B}}{\sum_{c'} X_{c'}} \tag{42}$$

$$\alpha_{Bc} = \alpha_{cB} = \frac{\sum_a X_a \alpha_{B,ca}}{\sum_{a'} X_{a'}} \tag{43}$$

$$\alpha_{Ba} = \alpha_{aB} = \frac{\sum_c X_c \alpha_{B,ca}}{\sum_{c'} X_{c'}}$$

$$(44)$$

$$\tau_{cB} = -\frac{\ln G_{cB}}{\alpha_{cB}}$$

$$(45)$$

$$\tau_{aB} = -\frac{\ln G_{aB}}{\alpha_{cB}}$$

$$(46)$$

$$\tau_{Ba,ca} = \tau_{aB} - \tau_{ca,B} + \tau_{B,ca}$$

$$(47)$$

$$\tau_{Bc,ac} = \tau_{cB} - \tau_{ca,B} + \tau_{B,ca}$$

$$(48)$$

Parameters

The model adjustable parameters include:

- Pure component dielectric constant coefficient of nonaqueous solvents

- Born radius of ionic species

- NRTL interaction parameters for molecule-molecule, molecule-electrolyte, and electrolyte-electrolyte pairs

Note that for the electrolyte-electrolyte pair parameters, the two electrolytes must share either one common cation or one common anion.

Each type of the electrolyte NRTL parameter consists of both the nonrandomness factor, α, and energy parameters, τ.

The pure component dielectric constant coefficients of nonaqueous solvents and Born radius of ionic species are required only for mixed-solvent electrolyte systems.

The temperature dependency relations of these parameters are given in Electrolyte NRTL Activity Coefficient Model.

Heat of mixing is calculated from temperature derivatives of activity coefficients. Heat capacity is calculated from secondary temperature derivative of the activity coefficient. As a result, the temperature dependent parameters are critical for modeling enthalpy correctly. It is recommended that enthalpy data and heat capacity data be used to obtain these temperature dependency parameters. See also Electrolyte NRTL Enthalpy and Electrolyte NRTL Gibbs Energy.

Obtaining Parameters

In the absence of electrolytes, the electrolyte NRTL model reduces to the NRTL equation which is widely used for non-electrolyte systems. Therefore, molecule-molecule binary parameters can be obtained from binary nonelectrolyte systems.

Electrolyte-molecule pair parameters can be obtained from data regression of apparent single electrolyte systems.

Electrolyte-electrolyte pair parameters are required only for mixed electrolytes with a common ion. Electrolyte-electrolyte pair parameters can affect trace ionic activity precipitation. Electrolyte-electrolyte pair parameters can be obtained by regressing solubility data of multiple component electrolyte systems.

When the electrolyte-molecule and electrolyte-electrolyte pair parameters are zero, the electrolyte NRTL model reduces to the Debije-Hückel limiting law. Calculation results with electrolyte-molecule and electrolyte-electrolyte pair parameters fixed to zero should be adequate for very dilute weak electrolyte systems; however, for concentrated systems, pair parameters are required for accurate representation.

See *Physical Property Data*, Chapter 1, for the pair parameters available from the electrolyte NRTL model databank. The table contains pair parameters for some electrolytes in aqueous solution at 100°C. These values were obtained by using the Aspen Physical Property Data Regression System (DRS) to regress vapor pressure and mole fraction data at T=100°C with SYSOP15S (Handbook of Chemistry and Physics, 1975). In running the DRS, standard deviations for the temperature (°C), vapor pressure (mmHg), and mole fractions were set at 0.2, 1.0, and 0.001, respectively. In addition, complete dissociation of the electrolyte was assumed for all cases.

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Pitzer Activity Coefficient Model

Overview

The Pitzer model was developed as an improvement upon an earlier model proposed by Guggenheim (1935, 1955). The earlier model worked well at low electrolyte concentrations, but contained discrepancies at higher concentrations (>0.1M). The Pitzer model resolved these discrepancies, without resorting to excessive arrays of higher-order terms.

The model can be used for aqueous electrolyte systems, up to 6 molal ionic strength. It cannot be used for mixed solvent electrolyte systems.

This appendix provides theoretical background for the model. All model equations are included. Parameter requirements are discussed in Pitzer Activity Coefficient Model.

Model Development

The Pitzer model analyzes "hard-core" effects in the Debije-Hückel theory. It uses the following expansion as a radial distribution function:

$$g_{ij}(r) = 1 - q_{ij}(r) + \tfrac{1}{2} q_{ij}^2(r) \tag{1}$$

Where:

g_{ij}	=	Distribution function
r	=	Radius
q_{ij}	=	$z_i Q_e \dfrac{\Psi_j(r)}{kT}$ (pair potential of mean force)

With:

z_i	=	Charge of ion i
Q_e	=	Electron charge
$\Psi_j(r)$	=	Average electric potential for ion j
k	=	Boltzmann's constant
T	=	Temperature

This radial distribution function is used in the so-called pressure equation that relates this function and the intermolecular potential to thermodynamic properties. From this relation you can obtain an expression for the osmotic coefficient.

Pitzer proposes a general equation for the excess Gibbs energy. The basic equation is:

$$\frac{G^E}{n_w RT} = f(1) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \tag{2}$$

Where:

G^E	=	Excess Gibbs energy
R	=	Gas constant
T	=	Temperature
n_w	=	Kilograms of water
m_i	=	$\dfrac{x_i}{x_w}\left(\dfrac{M_w}{1000}\right) = \dfrac{n_i}{n_w}$ (molality of ion i)

With:

x_i	=	Mole fraction of ion i
x_w	=	Mole fraction of water
M_w	=	Molecular weight of water (g/mol)
n_i	=	Moles of ion i

The function f(I) is an electrostatic term that expresses the effect of long-range electrostatic forces between ions. This takes into account the hard-core effects of the Debije-Hückel theory. This term is discussed in detail in the following section. The parameters λ_{ij} are second virial coefficients that account for the short-range forces between solutes i and j. The parameters μ_{ijk} account for the interactions between solutes, i, j, k. For ion-ion interactions, λ_{ij} is

a function of ionic strength. For molecule-ion or molecule-molecule interactions this ionic strength dependency is neglected.

The dependence of μ_{ijk} on ionic strength is always neglected. The matrices λ_{ij} and μ_{ijk} are also taken to be symmetric (that is, $\lambda_{ij} = \lambda_{ji}$).

Pitzer modified this expression for the Gibbs energy by identifying combinations of functions. He developed interaction parameters that can be evaluated using experimental data. He selected mathematical expressions for these parameters that best fit experimental data.

Pitzer's model can be applied to aqueous systems of strong electrolytes and to aqueous systems of weak electrolytes with molecular solutes. These applications are discussed in the following section.

Application of the Pitzer Model to Aqueous Strong Electrolyte Systems

Pitzer modified his basic equation to make it more useful for data correlation of aqueous strong electrolytes. He defined a set of more directly observable parameters to represent combinations of the second and third virial coefficients. The modified Pitzer equation is:

$$\frac{G^e}{RT} = n_w \left[\begin{array}{c} f(I) + 2\sum_c \sum_a m_c m_a \left(B_{ca} + \left(\sum_c m_c |z_c| \right) C_{ca} \right) \\ + \sum_c \sum_{c'} m_c m_{c'} \left(\theta_{cc'} + \frac{\sum_a m_a \Psi_{cc'a}}{2} \right) + \sum_a \sum_{a'} m_a m_{a'} \left(\theta_{aa'} + \frac{\sum_c m_c \Psi_{caa'}}{2} \right) \end{array} \right] \quad (3)$$

z_i　　　=　　Charge of ion i

Subscripts c, c', and a, a' denote cations and anions of the solution. B, C, θ, and Ψ are interaction parameters. $f(I)$ is an electrostatic term as a function of ionic strength. The cation-anion parameters B and C are characteristic for an aqueous single-electrolyte system. These parameters can be determined by the properties of pure (apparent) electrolytes. B is expressed as a function of $\beta^{(0)}$ and $\beta^{(1)}$ or $\beta^{(0)}$, $\beta^{(2)}$ and $\beta^{(3)}$ (see equations 11 through 15).

The parameters θ and Ψ are for the difference of interaction of unlike ions of the same sign from the mean of like ions. These

parameters can be measured from common-ion mixtures. Examples are $NaCl + KCl + H_2O$ or $NaCl + NaNO_3 + H_2O$ (sic, Pitzer, 1989). These terms are discussed in detail later in subsequent sections of this chapter.

Fürst and Renon (1982) propose the following expression as the Pitzer equation for the excess Gibbs energy:

$$\frac{G^E}{RT} = n_w \left[\begin{array}{l} f(I) + \sum_i \sum_j B_{ij} m_i m_j + \sum_i \sum_j \theta_{ij} m_i m_j + \frac{1}{2} \sum_i \sum_j \left(\sum_k m_k |z_k| \right) C_{ij} m_i m_j \\ + \frac{1}{6} \sum_i \sum_j \sum_k \Psi_{ijk} m_i m_j m_k \end{array} \right] \tag{4}$$

The difference between equations 3 and 4 is that Pitzer orders cation before anions. Fürst and Renon do not. All summations are taken over all ions i and j (both cations and anions). This involves making the parameter matrices B_{ij}, C_{ij}, θ_{ij}, and Ψ_{ijk} symmetric, as follows:

Second-order parameters are written B_{ij} if i and j are ions of different sign. $B_{ij} = 0$ if the sign of z_i = sign of z_j, and $B_{ii} = 0$. Since cations are not ordered before anions, $B_{ij} = B_{ji}$. This eliminates the 2 in the second term in brackets in Pitzer's original expression (equation 3). Second-order parameters are written θ_{ij} if i and j are ions of the same sign. Thus $\theta_{ij} = 0$ if the sign of z_i is different from the sign of z_j, and $\theta_{ii} = 0$ with $\theta_{ij} = \theta_{ji}$.

Third-order parameters are written C_{ij} if i and j are ions with different signs. $C_{ij} = 0$ if the sign of z_i = sign of z_i, and $C_{ii} = 0$ with $C_{ij} = C_{ji}$. The factor of 2 in the fifth bracketed term in Pitzer's original expression (equation 3) becomes 1/2 in equation 4. The matrix C is symmetric and $\sum m_k |z_k|$ is extended to all ions to make the equation symmetric.

Ψ_{ijk} is written for three different ions $\Psi_{ijk} = \Psi_{kij} = \Psi_{jki}$, and $\Psi_{ikk} = 0$. $\Psi_{ijk} = 0$ if the sign of z_i =sign of z_i =sign of z_k. The factor of 1/6 is different from 1/2 in the last term in brackets in Pitzer's original expression. Pitzer distinguishes between cations and anions. In Pitzer's original model this parameter appears twice, as $\Psi_{cc'a}$ and $\Psi_{c'ca}$. In this modified model, it appears six times, as $\Psi_{cc'a}$, $\Psi_{c'ca}$, $\Psi_{acc'}$, $\Psi_{ac'c}$, $\Psi_{cac'}$ and $\Psi_{c'ac}$. Fürst and Renon's

expression, equation 4, calculates the expressions for activity coefficients and osmotic coefficients.

Calculation of Activity Coefficients

The natural logarithm of the activity coefficient for ions is calculated from equation 4 to give:

$$\ln\gamma_{m,i}^* = \frac{\partial\left(\dfrac{G^E}{RT}\right)}{\partial n_i} \qquad (5)$$

$$= \tfrac{1}{2}z_i^2 f' + 2\sum_j m_j B_{ij} + \tfrac{1}{2}z_i^2\sum_i\sum_k \mathrm{B}_{ij'}m_j m_k$$

$$+ 2\sum_j \theta_{ij}m_j + \tfrac{1}{2}|z_i|\sum_j\sum_k C_{jk}m_j m_k$$

$$+ \sum_j\left(\sum_k m_k|z_k|\right)C_{ij}m_j + \tfrac{1}{2}\sum_j\sum_k \Psi_{ijk}m_j m_k$$

Where θ' is neglected.

For water the logarithm of the activity coefficient is calculated similarly, as follows:

Applying:

$$\ln\gamma_{m,w} = \frac{\partial\left(\dfrac{G^E}{RT}\right)}{\partial n_w}$$

to equation 3 and using:

$$n_w = \frac{N_w M_w}{1000}$$

Where N_w moles water, gives:

$$\frac{1000}{M_w}\ln\gamma_{m,w} = f - If' - \sum_i\sum_j m_i m_j B_{ij} - \sum_i\sum_j B_{ij'}I - \sum_i\sum_j m_i m_j\theta_{ij} \qquad (6)$$

$$- \sum_i\sum_j \Sigma_k m_k|z_k|m_i m_j C_{ij} - \tfrac{1}{3}\sum_i\sum_j\sum_k m_i m_j m_k\Psi_{ijk}$$

f(I), the electrostatic term, is expressed as a function of ionic strength I :

$$f(I) = -A_\varphi\left(\frac{4I}{b}\right)\left[\ln\left(1+bI^{1/2}\right)\right] \qquad (7)$$

I, the ionic strength, is defined as:

$$I = \frac{1}{2} \sum_i m_i z_i^2 \tag{8}$$

Taking the derivative of equation 7 with respect to I, gives:

$$f'(I) = \frac{df}{dI} = -2A_\varphi \left[\frac{I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} + \frac{2}{b} \ln\left(1 + bI^{\frac{1}{2}}\right) \right] \tag{9}$$

So that:

$$f - If' = \frac{-2A_\varphi I^{\frac{3}{2}}}{1 + bI^{\frac{1}{2}}} \tag{10}$$

This equation is used in equation 6. In equations 7 and 9, is the usual Debije-Hückel constant for the osmotic coefficient, determined from:

$$A_\varphi = \frac{1}{3} \left(\frac{2\pi N_A d_w}{1000} \right)^{\frac{1}{2}} \left(\frac{Q_e^2}{\varepsilon_B kT} \right)^{\frac{3}{2}} \tag{11}$$

Where:

N_A	=	Avogadro's constant
d_w	=	Water density
ε_B	=	Dielectric constant of solvent B

b is an adjustable parameter, which has been optimized in this model to equal 1.2.

B and B' need expressions so that equations 5 and 6 can completely be solved for the activity coefficients. The parameter B is determined differently for different electrolyte pairings. For 1-n electrolytes (1-1, 1-2, 2-1, and so on) the following expression gives the parameter B:

$$B = \beta_{ij}^{(0)} + \frac{2\beta_{ij}^{(1)}}{\alpha_1^2 I} \left[1 - \left(1 + \alpha_1 I^{\frac{1}{2}}\right) e^{\left(-\alpha_1 I^{\frac{1}{2}}\right)} \right] \tag{12}$$

with $\alpha_1 = 2.0$.

For 2-2 electrolytes, B is determined by the following expression:

$$B = \beta_{ij}^{(0)} + \frac{2\beta_{ij}^{(2)}}{\alpha_2^2 I} \left[1 - \left(1 + \alpha_2 I^{\frac{1}{2}}\right) e^{\left(-\alpha_2 I^{\frac{1}{2}}\right)} \right] + \frac{2\beta_{ij}^{(3)}}{\alpha_3^2 I} \left[1 - \left(1 + \alpha_3 I^{\frac{1}{2}}\right) e^{\left(-\alpha_3 I^{\frac{1}{2}}\right)} \right] \tag{13}$$

with $\alpha_2 = 12.0$ and $\alpha_3 = 1.4$.

By taking appropriate derivatives, expressions for B' can be derived for $1 - n$ electrolytes:

$$B' = \frac{2\beta^{(1)}}{4I^2}\left[-1+\left(1+2I^{\frac{1}{2}}+2I\right)e^{\left(-2I^{\frac{1}{2}}\right)}\right] \tag{14}$$

and for 2-2 electrolytes:

$$B' = \frac{2\beta^{(2)}}{144I^2}\left[-1+\left(1+12I^2+72I\right)e^{\left(-12I^{\frac{1}{2}}\right)}\right]$$
$$+ \frac{2\beta^{(3)}}{(1.4)^2 I^2}\left[-1+\left(1+1.4I^{\frac{1}{2}}+\frac{(1.4)^2 I}{2}\right)e^{\left(-1.4I^{\frac{1}{2}}\right)}\right] \tag{15}$$

The parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$ and also C, θ, and Ψ can be found in Pitzer's articles .

After the activity coefficients are calculated, they can be converted to the mole fraction scale from the molality scale by the following relations:

For ions:

$$\gamma_{x,i} = \gamma_{m,i}\left(\frac{m_i}{x_i}\right)\left(\frac{M_w}{1000}\right) \tag{16}$$

For water:

$$\gamma_{x,w} = \frac{\gamma_{m,i}\exp\left(\frac{-\sum_i m_i M_w}{1000}\right)}{x_w} \tag{17}$$

Where:

γ_m	=	Activity coefficient (molality scale)
γ_x	=	Activity coefficient (mole fraction scale)

Application of the Pitzer Model to Aqueous Electrolyte Systems with Molecular Solutes

In aqueous weak electrolyte systems with molecular solutes, the second and third virial coefficients in the basic Pitzer equation for molecule-ion and molecule-molecule interactions must be considered. The following extensions of Pitzer's interaction parameters are made.

The second-order parameters B_{ij} are extended to include molecule-molecule and molecule-ion interaction parameters.

The third-order parameters Ψ_{ijk} are extended to molecule-molecule-molecule interactions. The following expressions relate Ψ_{ijk} to Pitzer's original μ_{ijk}:

$$\Psi_{iii} = 6\mu_{iii}$$

However, molecule-molecule interactions were not taken into account by Pitzer and coworkers. So μ_{iii} is an artificially introduced quantity.

The equations for activity coefficients and the Gibbs free energy are the same as equations 3 through 6.

Parameters

The Pitzer model in the Aspen Physical Property System involves user-supplied parameters. These parameters are used in the calculation of binary and ternary parameters for the electrolyte system. These parameters include the cation-anion parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$ and C^{Φ}, cation-cation parameter $\theta_{cc'}$, anion-anion parameter $\theta_{aa'}$, cation1-cation2-common anion parameter $\Psi_{cc'a}$, anion1-anion2-common cation parameter $\Psi_{caa'}$, and the molecule-ion and molecule-molecule parameters $\beta^{(0)}$, $\beta^{(1)}$ and, C^{Φ}. The parameter names in the Aspen Physical Property System and their requirements are discussed in Pitzer Activity Coefficient Model.

Parameter Conversion

For 2-2 electrolytes the parameter $\beta^{(3)}$ corresponds to Pitzer's $\beta^{(1)}$. $\beta^{(2)}$ is the same in both the Aspen Physical Property System and original Pitzer models. Pitzer refers to the 2-2 electrolyte parameters as $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(0)}$. $\beta^{(0)}$ and $\beta^{(2)}$ retain their meanings in both models, but Pitzer's $\beta^{(1)}$ is $\beta^{(3)}$ in the Aspen Physical Property System. Be careful to make this distinction when entering 2-2 electrolyte parameters.

Pitzer often gives values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$, and C^{Φ} that are corrected by some factors (see Pitzer and Mayorga (1973) for examples). These factors originate from one of Pitzer's earlier expressions for the excess Gibbs energy:

$$\frac{G^E}{n_w RT} = f^{G^E} + m^2 \left(2n_c n_a\right) B^{G^E} + m^3 \left[2\left(n_c n_a\right)^{3/2}\right]^{C_{ca}^{G^E}} \tag{18}$$

Where:

$$C_{ca}^{G^E} \quad = \quad 1/2\, C_{ca}^{\phi}$$

n_a =   Mole number of anions

n_c =   Mole number of cation

Here $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $\beta^{(3)}$ are multiplied by a factor of $2n_c n_a$.

C is multiplied by a factor of $2\left(n_c n_a\right)^{3/2}$.

Aspen Physical Property System accounts for these correcting factors. Enter the parameters without their correcting factors.

For example, Pitzer gives the values of parameters for $M_g Cl_2$ as:

$4/3\,\beta^{(0)}$ =   0.4698

$4/3\,\beta^{(1)}$ =   2.242

$\dfrac{2^{5/2}}{3} C^{\phi}$ =   0.00979

Perform the necessary conversions and enter the parameters as:

$\beta^{(0)}_{Mg^{2+},Cl^-}$ =   0.3524

$\beta^{(0)}_{Mg^{2+},Cl^-}$ =   1.6815

$C^{\phi}_{Mg^{2+},Cl^-}$ =   0.00520

Parameter Sources	Binary and ternary parameters for the Pitzer model for various electrolyte systems are available from Pitzer's series on the thermodynamics of electrolytes. These papers and the electrolyte parameters they give are:

Reference	**Parameters available**
(Pitzer, 1973)	Binary parameters $\left(\beta^{(0)}, \beta^{(1)}, C^{\phi}\right)$ for 13 dilute aqueous electrolytes
(Pitzer and Mayorga, 1973)	Binary parameters for 1-1 inorganic electrolytes, salts of carboxylic acids (1-1), tetraalkylammonium halids, sulfonic acids and salts, additional 1-1 organic salts, 2-1 inorganic compounds, 2-1 organic electrolytes, 3-1 electrolytes, 4-1 and 5-1 electrolytes
(Pitzer and Mayorga, 1974)	Binary parameters for 2-2 electrolytes in water at 25°C
(Pitzer and Kim, 1974)	Binary and ternary parameters for mixed electrolytes, binary mixtures without a common ion, mixed electrolytes with three or more solutes
(Pitzer, 1975)	Ternary parameters for systems mixing doubly and singly charged ions
(Pitzer and Silvester, 1976)	Parameters for phosphoric acid and its buffer solutions
(Pitzer, Roy and Silvester, 1977)	Parameters and thermodynamic properties for sulfuric acid
(Pitzer and Silvester, 1977)	Data for NaCl and aqueous NaCl solutions
(Pitzer, Silvester, and Peterson, 1978)	Rare earth chlorides, nitrates, and perchlorates
(Peiper and Pitzer, 1982)	Aqueous carbonate solutions, including mixtures of sodium carbonate, bicarbonate, and chloride
(Phutela and Pitzer, 1983)	Aqueous calcium chloride
(Pitzer, Conceicao, and deLima, 1983)	Saturated aqueous solutions, including mixtures of sodium chloride, potassium chloride, and cesium chloride

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