# Aspen Plus®

**STEADY STATE SIMULATION**

Version 10

## Physical Property Methods and Models

REFERENCE MANUAL

AspenTech®

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# Contents

# About this Manual

This manual provides an overview of Aspen Plus physical property methods and detailed technical reference information on property methods (option sets), property calculation methods and routes, property models, and parameter estimation. It 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*.

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**Aspen Plus Getting Started Modeling Petroleum Processes**   This tutorial includes several hands-on sessions to familiarize you with simulating petroleum processes with Aspen Plus.

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**Aspen Plus reference manual series**   Aspen Plus reference manuals provide detailed technical reference information. These manuals include background information about the unit operation models and the physical properties methods and models available in Aspen Plus, tables of Aspen Plus databank parameters, group contribution method functional groups, and a wide range of other reference information. The set comprises:

- *Unit Operation Models*
- *Physical Property Methods and Models*
- *Physical Property Data*
- *User Models*
- *System Management*
- *System Administration*
- *Summary File Toolkit*

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# 1      Overview of Aspen Plus Property Methods

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 simulation 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 on page 1-38 for definitions of thesymbols used in equations.

# Thermodynamic Property Methods

The key thermodynamic property calculation performed in a simulation 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:

$\alpha$     =     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 $\varphi_i^\alpha$ 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:

$$f_i^v \quad = \quad \varphi_i^v y_i p \tag{5}$$

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

Where $\varphi_i^v$ is calculated according to equation 4,

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

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

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

Each property method in Aspen Plus 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:

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

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

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

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

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

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

An equation of state describes the pressure, volume and temperature ($p, V, T$) behavior of pure components and mixtures. Usually it is explicit in pressure. Most equations of state have different terms to represent attractive and repulsive forces between molecules. Any thermodynamic property, such as fugacity coefficients and enthalpies, can be calculated from the equation of state. Equation-of-state properties are calculated relative to the ideal gas properties of the same mixture at the same conditions. See Calculation of Properties Using an Equation-of-State Property Method on page 1-7.

## 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 on page 1-7). The calculation is the same for supercritical and subcritical components (see Activity Coefficient Method on page 1-10).

## 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 $\varphi_i^v$ and $\varphi_i^l$. 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 on page 1-22).
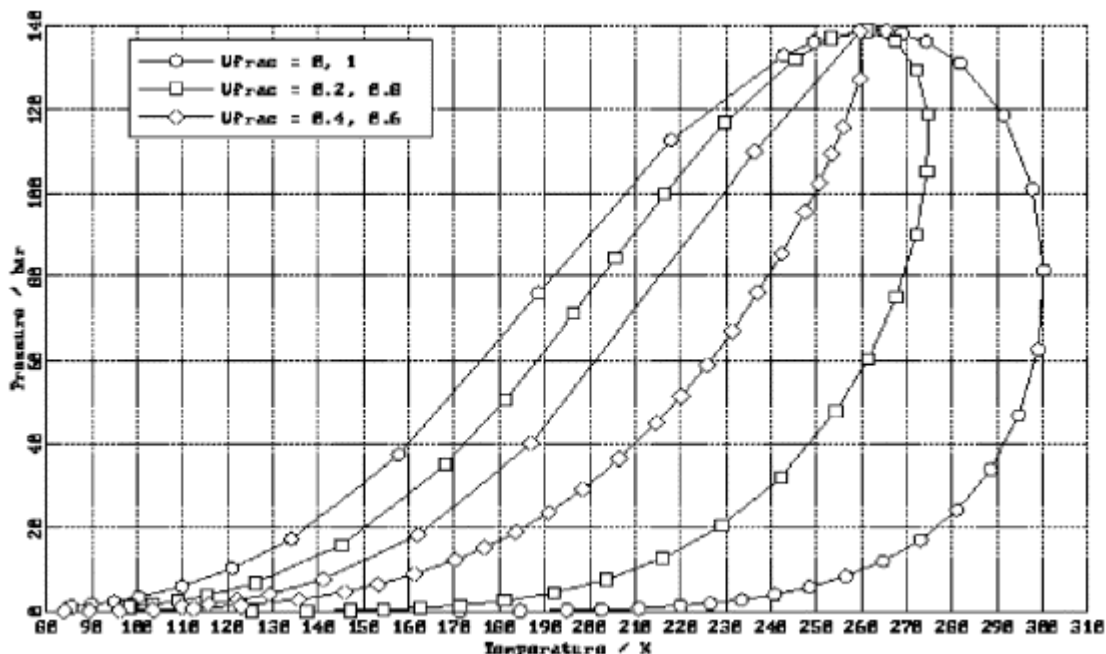


***Phase Envelope of a Methane-Rich Hydrocarbon Mixture***

### 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 on page 1-10, 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:

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

- Entropy departure:

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

- Gibbs energy departure:

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

- 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 $p(T, V_m)$ for $V_m$ or computed by an empirical correlation.

## Advantages and Disadvantages of the Equation-of-State Method

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

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

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.

## References

A.J. Davenport and J.S. Rowlinson, *Trans. Faraday Soc.*, Vol. 59 (1963), p. 78, (cited after van der Kooi, 1981).

D.E.L. Dyke, J.S. Rowlinson and R. Thacker, *Trans. Faraday Soc.*, Vol. 55, (1959), p. 903, (cited after Rowlinson and Swinton, 1982).

D.J. Fall, J.L. Fall, and K.D. Luks, "Liquid-liquid-vapor immiscibility Limits in Carbon Dioxide + n-Paraffin Mixtures," *J. Chem. Eng. Data*, Vol. 30, No. 1, (1985), pp. 82-88.

L. Haar, J.S. Gallagher, and J.H. Kell, *NBSINRC Steam Tables* (Washington: Hemisphere Publishing Corporation, 1984).

C.P. Hicks and C.L. Young, *Trans. Faraday Soc.*, Vol. 67, (1971), p.1605, (cited after Rowlinson and Swinton, 1982).

J.P. Kohn, *AIChE J.*, Vol 7, (1961), p. 514, (cited after van der Kooi, 1981).

H.J. van der Kooi, *Metingen en berekeningen aan het systeem methaan-n-eiscosaan*, Ph.D. thesis, Delft University of Technology (Delft: Delftse Universitaire Pers, 1981) (In Dutch).

C.J. Peters, R.N. Lichtenthaler, and J. de Swaan Arons, "Three Phase Equilibria In Binary Mixtures Of Ethane And Higher N-Alkanes," *Fluid Phase Eq.*, Vol. 29, (1986), pp. 495-504.

M.E. Pozo and W.B. Street, "Fluid Phase Equilibria for the System Dimethyl Ether/Water from 50 to 200 C and Pressures to 50.9 MPa," *J. Chem. Eng. Data*, Vol. 29, No. 3, (1984), pp. 324-329.

J.S. Rowlinson and F.L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed. (London, etc.:Butterworths, 1982), ch. 6.

# 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 $\gamma_i$ 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 $\gamma_i$ 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 on page 1-3). These forms of ideality can be used next to each other.

In the majority of mixtures, $\gamma_i$ 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 $\gamma_i$ 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 $\varphi_i^v$ is computed from an equation of state (see Equation-of-State Methodon page 1-3). The liquid activity coefficient $\gamma_i$ 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 $\gamma_i$ 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 |
| | = | $\exp\left(\dfrac{1}{RT}\int_{p_i^{*,l}}^{p} V_i^{*,l} dp\right)$ |

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 $\gamma_i$ is converted to the infinite dilution reference state through the relationship

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

Where:

| | | |
|---|---|---|
| $\gamma_i^\infty$ | = | The infinite dilution activity coefficient of component $i$ in the mixture |

By this definition $\gamma_i^*$ 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 on page 1-33.

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:

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

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

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

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

For the computation of the different terms in equations 31 and 32, see Vapor-Liquid Equilibria on page 1-4.

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 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 on page 1-33. 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:
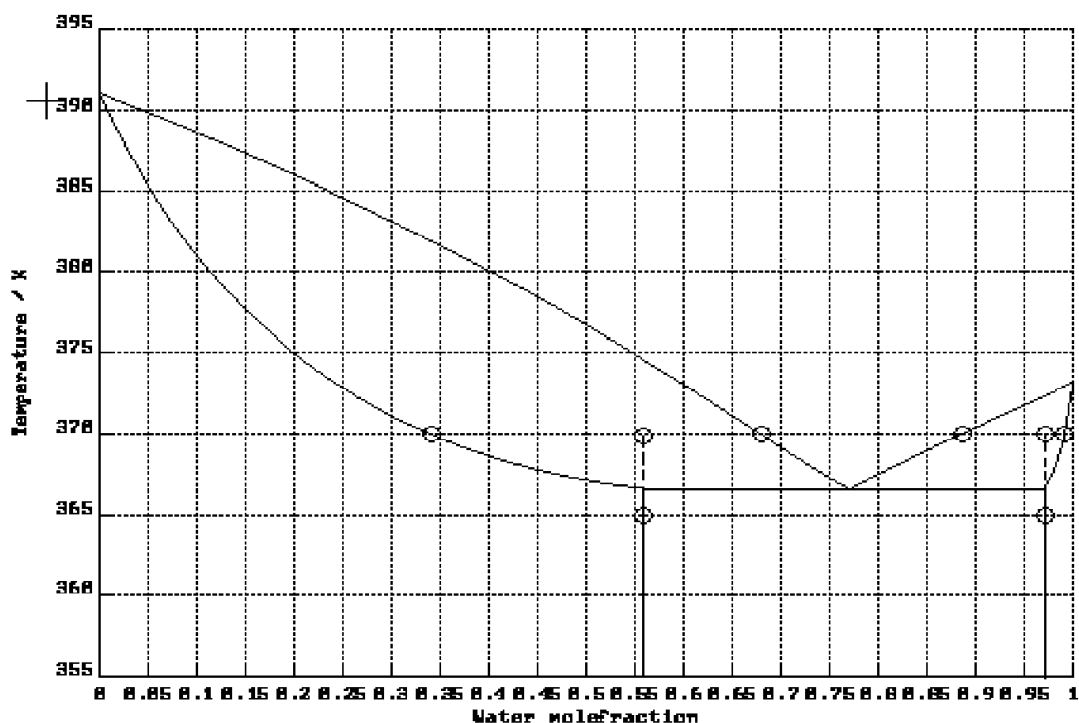


***(T,x,x,y)—Diagram of Water and Butanol-1 at 1.01325 bar***

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[1]. 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.
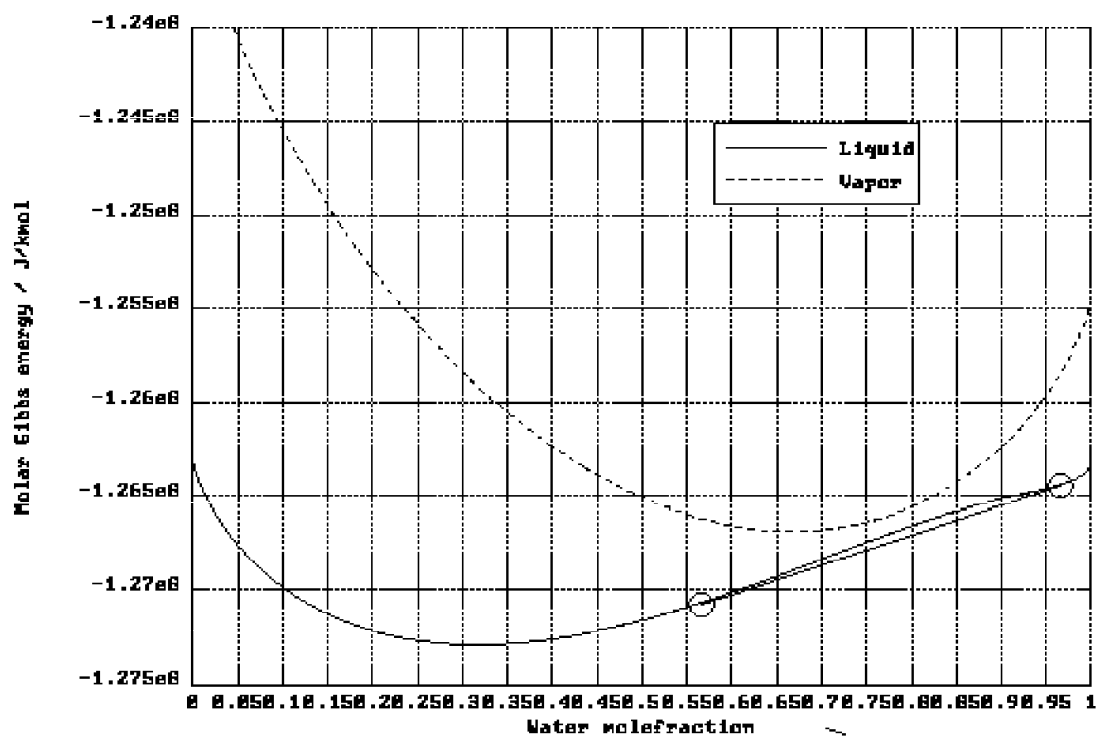


**Molar Gibbs Energy of Butanol-1 and Water at 365 K and 1 atm**

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.
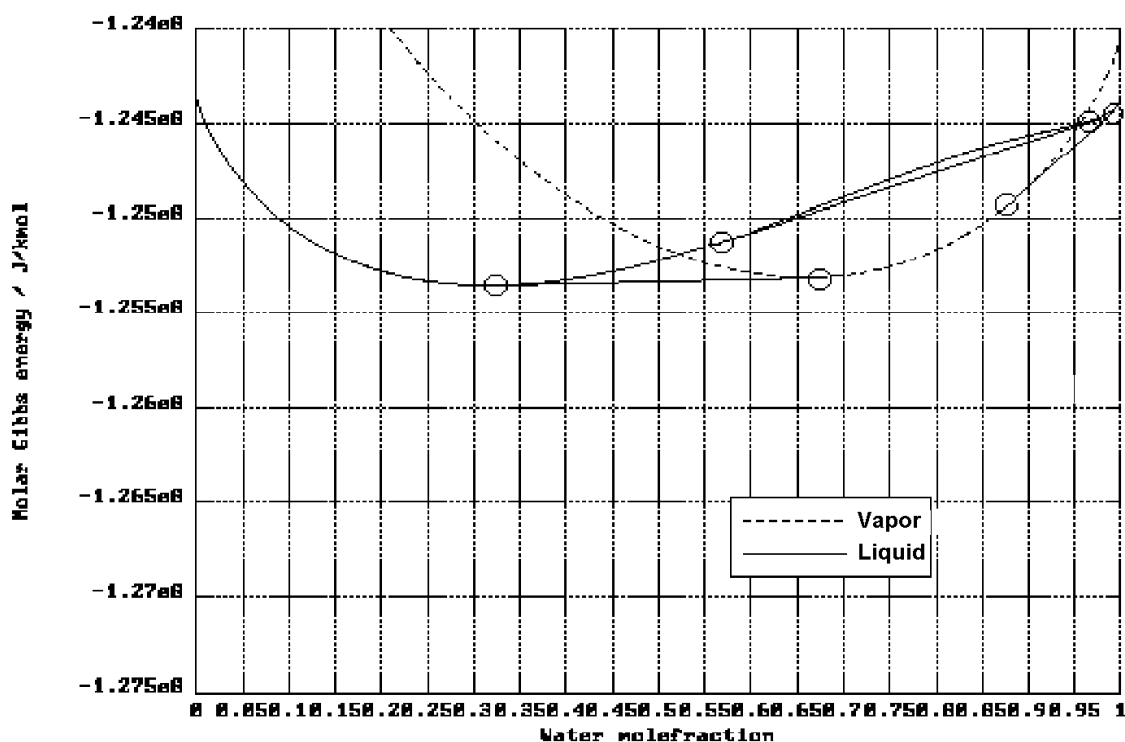


***Molar Gibbs Energy of Butanol-1 and Water at 370 K and 1 atm***

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 on page 1-33). 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 Equilibria on page 1-6) As a result, the analog of equation 31 holds:

$$x_i^{l1}\gamma_i^{l1}f_i^{*,l} = x_i^{l2}\gamma_i^{l2}f_i^{*,l} =...x_i^{s1}\gamma_i^{s1}f_i^{*,s} = x_i^{s2}\gamma_i^{s2}f_i^{*,s} =...\varphi_i^{v}y_ip \tag{33}$$

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 7, 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[2]. 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.
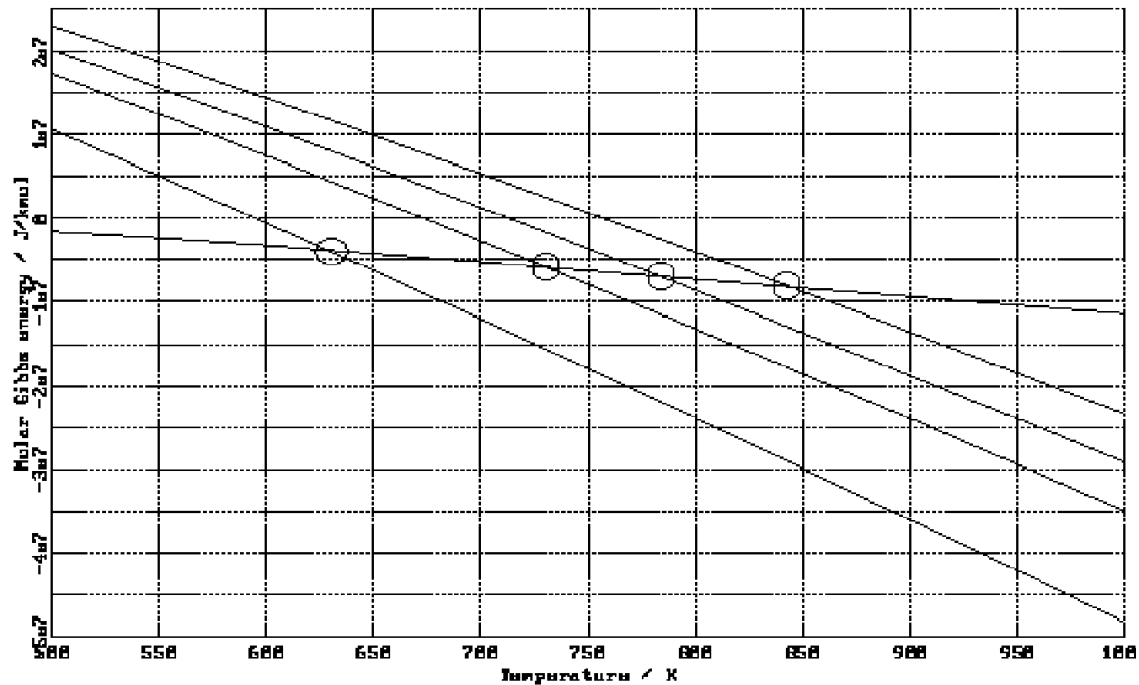
**Thermodynamic Potential of Mercury at 7, 5, 10, and 20 bar**
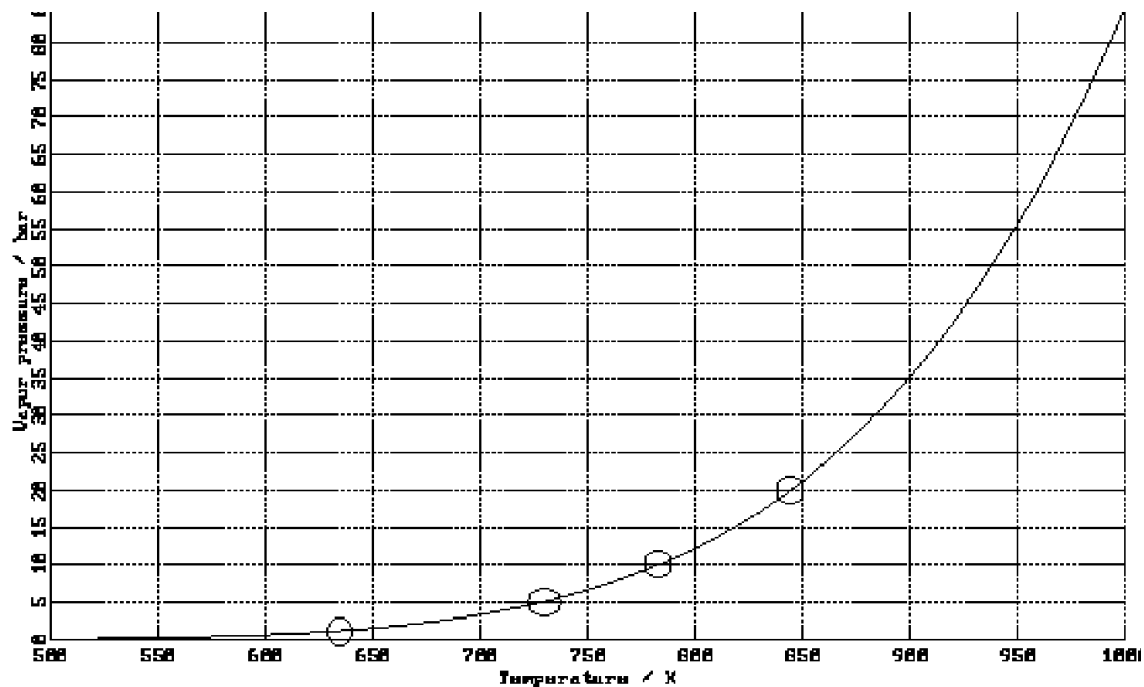


**Vapor Pressure Curve of Liquid Mercury**

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 on page 1-4). 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.

## Calculation of Other Properties Using Activity Coefficients

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

**Vapor phase:** Vapor enthalpy, entropy, Gibbs energy and density are computed from an equation of state (see Calculation of Properties Using an Equation-of-State Property Method on page 1-7).

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

$$S_m^s = \frac{1}{T}\left(H_m^s - G_m^s\right)$$ (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 Aspen Plus for a large number of component pairs. These binary parameters are used automatically. See *Aspen Plus 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.

### References

Collection, Aliphatic Hydrocarbons, C4 - C6, *Chemistry Data Series Vol 1, Part 6a*, D. Bierens and R.Eckerman, eds., (Frankfurt/Main: Dechema, 1980).

J. Gmehling, U. Onken and W. Arlt, "Vapor-Liquid Equilibrium Data Collection, Aqueous-Organic Systems, Supplement 2," *Chemistry Data Series Vol 1, Part 1b*, D. Bierens and R.Eckerman, eds., (Frankfurt/Main: Dechema, 1988).

H.A.J. Oonk, *Phase Theory, The Thermodynamics of Heterogeneous Equilibria*, (Amsterdam, etc.: Elsevier Scientific Publishing Company, 1981), Ch. 4.

# Equation-of-State Models

The simplest equation of state is the ideal gas law:

$$p = \frac{RT}{V_m}$$ (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 on page 1-10).

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 $\frac{1}{r^6}$, 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, 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 Aspen Plus. The original Redlich-Kwong-Soave and Peng-Robinson equations will be called standard cubic equations of state. Cubic equations of state in Aspen Plus 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 Aspen Plus*

| 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 Aspen Plus: 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:

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

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

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 Aspen Plus). 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 on page 1-33). The quality of the VLE predictions is good.

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

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

## Virial Equations of State

Virial equations of state in Aspen Plus 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:

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

Truncation of equation 49 after the second term and the use of the second virial coefficient $B$ can describe the behavior of gases up to several bar. The Hayden-O'Connell equation of state uses a complex computation of $B$ to account for the association and chemical bonding in the vapor phase (see Vapor Phase Association on page 1-27).

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

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

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

## Vapor Phase Association

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

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

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

The equilibrium constant of a dimerization reaction

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

in the vapor phase is defined in terms of fugacities:

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

With:

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

and realizing that $\varphi_i^v$ is approximately unity at low pressures:

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

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

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

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).
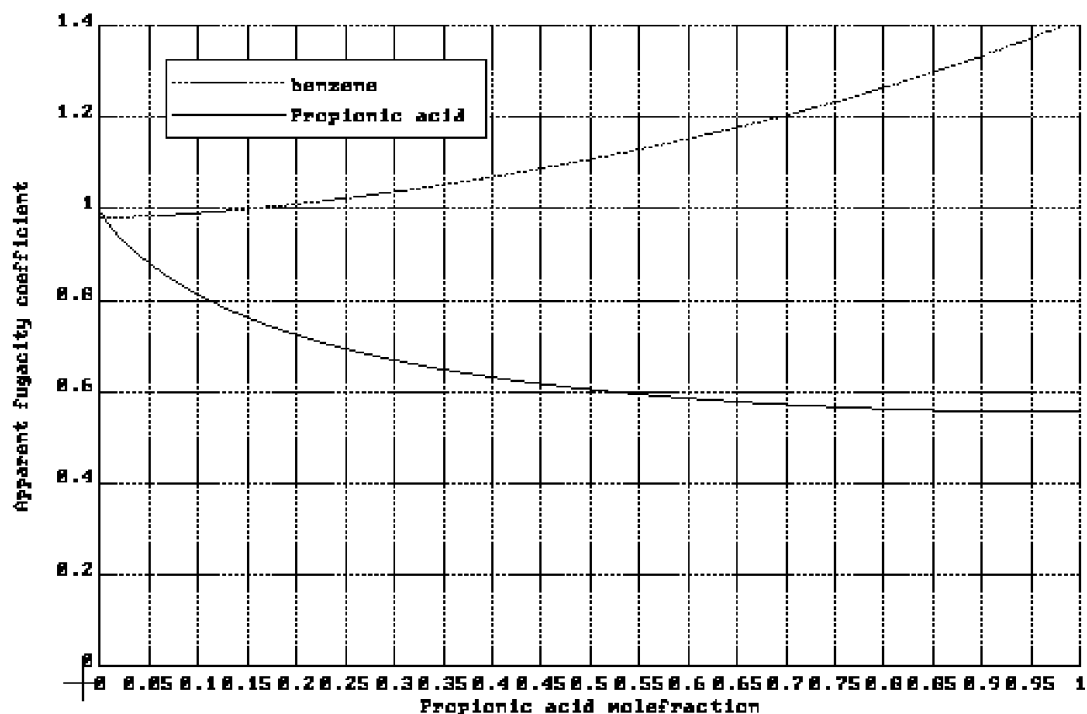


*Apparent Fugacity of Vapor Benzene and Propionic Acid*

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:

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

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.
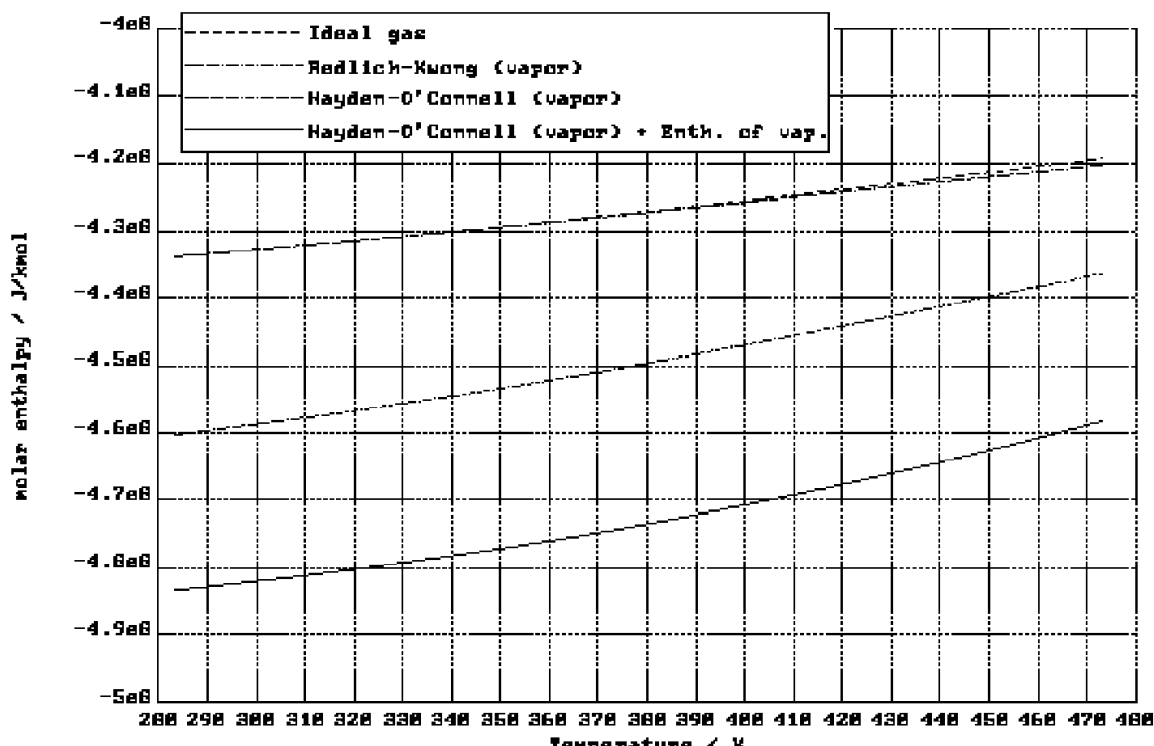


*Liquid and Vapor Enthalpy of Acetic Acid*

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 Aspen Plus.

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 Aspen Plus). $d$ and $p$ are adjustable parameters. Many values for $d$ and $p$ are available in the Nothnagel equation of state in Aspen Plus. 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 $\eta$. Pure component and binary values for $\eta$ are available in Aspen Plus.

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.

## References

M. M. Abbott and M. C. Van Ness, "Thermodynamics of Solutions Containing Reactive Species: A Guide to Fundamentals and Applications," *Fluid Phase Equilibria*, Vol 77, (1992), pp. 53-119.

A. Bondi, "Physical Properties of Moelcular Liquids, Crystals, and Glasses," Wiley, New York, 1968.

M.R. Brulé, C.T. Lin, L.L. Lee, and K.E. Starling, "Multiparameter Corresponding States Correlation of Coal-Fluid Thermodynamic Properties," *AIChE J.*, Vol. 28, No. 4, (1982), pp. 616 – 637.

S. Dahl and M.L. Michelsen, "High-Pressure Vapor-Liquid Equilibrium with a UNIFAC-based Equation of State", *AIChE J.*, Vol. 36, No. 12 (1990), pp. 1829-1836.

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

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, (1975), pp. 209-216.

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

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.

V.V. de Leeuw and S. Watanasiri, " Modelling Phase Equilibria And Enthalpies Of The System Water And Hydrofluoric Acid Using A 'HF Equation Of State' In Conjunction With The Electrolyte NRTL Activity Coefficient Model," Presented at the 13th European Seminar on Applied Thermodynamics, 9th-12th June 1993, Carry-le-Rouet, France.

Ch. Lermite and J. Vidal, "Les règles de mélange appliquées aux équations d'état." Revue de l'Institut Français du Pétrole, Vol. 43, No. 1, (1988), pp. 73-94.

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

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

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.

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

J.M. Prausnitz, R.N. Lichtenthaler, and E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria,* 2nd ed., (Englewood Cliffs: Prentice-Hall Inc., 1986), pp. 137-151.

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.

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

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.

# 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 on page 1-10).

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 on page 1-10) 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 Aspen Plus. 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 Aspen Plus. 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 (for literature references, see 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 (for literature references, see 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 *Aspen Plus 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 (for literature references, see Appendix A). A correlation is used to calculate the interaction parameters. The model is limited in accuracy, but predictive.

## References

Aa. Fredenslund, R.L. Jones, and J.M. Prausnitz, "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," *AIChE J.*, Vol. 21, (1975), pp. 1086-1099.

Aa. Fredenslund, J. Gmehling, and P. Rasmussen , *Vapor-Liquid Equilibria Using UNIFAC*, (Amsterdam: Elsevier, 1977).

B.L. Larsen, P. Rasmussen, and Aa. Fredenslund, "A Modified UNIFAC Group-Contribution Model for the Prediction of Phase Equilibria and Heats of Mixing," *Ind. Eng. Chem. Res.*, Vol. 26, (1987), pp. 2274-2286.

J.M. Prausnitz, R.N. Lichtenthaler, and E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria,* 2nd ed., (Englewood Cliffs: Prentice-Hall Inc., 1986), pp. 137-151.

U. Weidlich and J. Gmehling, "A Modified UNIFAC Model. 1. Prediction of VLE, $h^E$ , $\gamma^\infty$ ," *Ind. Eng. Chem. Res.*, Vol. 26, (1987), pp. 1372-1381.

# Transport Property Methods

Aspen Plus 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 Plus 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.

## References

R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties Of Gases And Liquids*, 4th ed., (New York, etc: McGraw-Hill Book Company, 1987).

# 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

### Symbol Definitions

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

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

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

# Footnotes

[1]    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).

**2**  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.

# 2 Property Method Descriptions

This chapter describes the Aspen Plus property methods. Topics include:

- Classification of property methods
- Recommended use
- Property method descriptions, organized by application

Since Aspen Plus 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 simulation. 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 |

*Continued*

## Refinery

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

## Gas Processing

| Application | Recommended Property Method |
|---|---|
| Hydrocarbon separations Demethanizer C3-splitter | Equations of state for high pressure hydrocarbon applications (with $k_{ij}$) |
| Cryogenic gas processing Air separation | Equations of state for high pressure hydrocarbon applications Flexible and predictive equations of state |
| Gas dehydration with glycols | Flexible and predictive equations of state |
| Acid gas absorption with<br>  Methanol (rectisol)<br>  NMP (purisol) | Flexible and predictive equations of state |
| Acid gas absorption with<br>  Water<br>  Ammonia<br>  Amines<br>  Amines + methanol (amisol)<br>  Caustic<br>  Lime<br>  Hot carbonate | Electrolyte activity coefficients |
| Claus process | Flexible and predictive equations of state |

## Petrochemicals

| Application | Recommended Property Method |
|---|---|
| Ethylene plant<br>  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 |

*Continued*

## Petrochemicals (continued)

| Application | Recommended Property Method |
| --- | --- |
| Aromatics<br>  BTX extraction | Liquid activity coefficients (very sensitive to parameters) |
| Substituted hydrocarbons<br>  VCM plant<br>  Acrylonitrile plant | Equations of state for high pressure hydrocarbon applications |
| Ether production<br>  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<br>  Alcohol separation | Liquid activity coefficients |
| Carboxylic acids<br>  Acetic acid plant | Liquid activity coefficients |
| Phenol plant | Liquid activity coefficients |
| Liquid phase reactions<br>  Estrification | Liquid activity coefficients |
| Ammonia plant | Equations of state for high pressure hydrocarbon applications (with $k_{ij}$) |
| Fluorochemicals | Liquid activity coefficients (and HF equation of state) |
| Inorganic Chemicals<br>  Caustic<br>  Acids<br>    Phosphoric acid<br>    Sulphuric acid<br>    Nitric acid<br>    Hydrochloric acid<br>    Hydrofluoric acid | Electrolyte activity coefficients<br><br><br><br><br><br>Electrolyte activity coefficient (and HF equation of state) |

## Coal Processing

| Application | Recommended Property Method |
| --- | --- |
| Size reduction<br>crushing, grinding | Solids processing (with coal analysis and particle size distribution) |
| Separation and cleaning<br>  sieving, cyclones,<br>  preciptition, washing | Solids processing (with coal analysis and and particle size distribution) |

*Continued*

**Coal Processing (continued)**

| Application | Recommended Property Method |
|---|---|
| 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 analyis with coal correlations) |
| Oil | (and assay analyis) |
| Steam cycles<br>  Compressors<br>  Turbines | Steam tables |
| Acid gas absorption | See Gas Processing earlier in this discussion. |

**Synthetic Fuel**

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

**Environmental**

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

*Continued*

**Environmental (continued)**

| Application | Recommended Property Method |
| --- | --- |
| Acid gas stripping from<br>  Water<br>  Ammonia<br>  Amines<br>  Amines + methanol (amisol)<br>  Caustic<br>  Lime<br>  Hot carbonate | Electrolyte activity coefficients |
| Claus process | Flexible and predictive equations of state |
| Acids<br>  Stripping<br>  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<br>crushing, grinding,<br>sieving, washing | Solids Processing (with inorganic databank) |
| Hydrometallurgy<br>  Mineral leaching | Electrolyte activity coefficients |
| Pyrometallurgy<br>  Smelter<br>  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 ($\chi = 1$)
- 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 on page 2-66 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 Plus contains an extensive collection of Henry's constants for many solutes in solvents. Solvents are water and other organic components. Aspen Plus 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<br>    Fugacity coefficient | Ideal gas law | |
| Enthalpy, entropy, Gibbs energy | Ideal gas heat capacity | CPIG or CPIGDP |
| Density | Ideal gas law | |
| Liquid mixture<br>    Fugacity coefficient | Ideal liquid activity 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) |

*Continued*

**Thermodynamic Properties (continued)**

| Properties | Models | Parameter Requirements |
|---|---|---|
| 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 on page 2-13 , Parameters Required for the GRAYSON Property Method on page 2-14 , Parameters Required for the PENG-ROB Property Method on page 2-16 , and Parameters Required for the RK-SOAVE Property Method on page 2-17 .

Parameter requirements for the common models are in the table labeled
Parameters Required for Common Models on page 2-18. 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 | Grayson-Streed liquid fugacity, Scatchard-Hildebrand activity coefficient |

**Petroleum-Tuned Equations of State**

| Property Method Name | Models |
|---|---|
| PENG-ROB | Peng-Robinson |
| RK-SOAVE | Redlich-Kwong-Soave |

**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.

## Range

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

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

The parameters for the Braun K-10 are all built-in. You do not need to supply them. See Parameters Required for Common Models on page 2-18 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 on page 2-13, and Parameters Required for Common Models on page 2-18

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

$$200 \quad < T \quad < 533 \text{ K}$$

$$0.5 \quad < T_{ri} \quad < 1.3$$

$$T_{rm} \quad < 0.93$$

$$P < 140 \text{ atm}$$

Where:

$$T_{ri} \quad = \quad \text{Reduced temperature of a component}$$

$T_{rm}$ = 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<br>  Fugacity coefficient,<br>  Density | Redlich-Kwong | TC, PC |
|   Enthalpy, entropy,<br>  Gibbs free energy | Ideal gas heat capacity,<br>Redlich-Kwong | CPIG or CPIGDP<br>TC, PC |
| Liquid mixture<br>  Fugacity coefficient,<br>  Gibbs free energy | Scatchard-Hildebrand activity coefficient | TC, DELTA, VLCVT1; GMSHVL |
| | Chao-Seader pure component fugacity<br>coefficient | TC, PC, OMEGA |

# GRAYSON

The GRAYSON property method uses the:

- Grayson-Streed correlation for reference state fugacity coefficients
- Scratchard-Hildllebrand 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

Refer to the tables labeled Parameters Required for the GRAYSON Property Method on page 2-14 and Parameters Required for Common Models for thermodynamic and transport property models, and their parameter requirements.

The GRAYSON property method is predictive. It can be used for crude towers, vacuum towers, and some parts of the ethylene process. It is recommended for systems containing hydrogen.

### Mixture Types

The GRAYSON property method was developed for systems containing hydrocarbons and light gases, such as carbon dioxide and hydrogen sulfide. It is recommended over the CHAO-SEA property method when the system contains hydrogen.

**Range**

Use the GRAYSON property method for systems with temperature and pressure limits of:

$200K < \text{T} < 700K$

$0.5 < T_{ri}$

$P < 210 \; atm$

Where:

| | | |
|---|---|---|
| $T_{ri}$ | = | Reduced temperature coefficient |

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 GRAYSON Property Method*

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

# 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 on page 2-16 and Parameters Required for Common Models on page 2-18 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 PLUS 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.

### *Parameters Required for the PENG-ROB Property Method*

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| Vapor mixture<br>  Fugacity coefficient<br>  Density | Peng-Robinson | TCPR or TC; PCPR or PC; OMGPR or OMEGA |
| Enthalpy, entropy,<br>Gibbs free energy | Ideal gas heat capacity,<br>Peng-Robinson | TCPR or TC; PCPR or PC; OMGPR or OMEGA<br>CPIG or CPIGDP |
| Liquid mixture<br>  Fugacity coefficient | Peng-Robinson | TCPR or TC; PCPR or PC; OMGPR or OMEGA CPIG or CPIGDP |
| Enthalpy, entropy,<br> Gibbs free energy | Ideal gas heat capacity,<br>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 on page 2-17 and Parameters Required for Common Models on page 2-18 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 Aspen Plus.

For accurate results in your VLE and LLE calculations, you must use binary parameters. You can use the Aspen Plus 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<br>  Fugacity coefficient,<br>  Density | Redlich-Kwong-Soave | TC, PC, OMEGA |
| Enthalpy, entropy<br>Gibbs free energy | Ideal gas heat capacity,<br>Redlich-Kwong-Soave | CPIG or CPIGDP,<br>TC, PC, OMEGA |
| Liquid mixture<br>  Fugacity coefficient | Redlich-Kwong-Soave | TC, PC, OMEGA |
| Enthalpy, entropy,<br>Gibbs free energy | Ideal gas heat capacity,<br>Redlich-Kwong-Soave | CPIG  or CPIGDP<br>TC, PC, OMEGA |

# Common Models

The following table lists the models used in all petroleum property methodsand 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, | Ideal heat capacity, | (CPIG or CPIGDP) |
|   Entropy | Lee-Kesler | 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) <br> MW, MUP, (STKPAR or LJPAR), VC |
|   Diffusivity | Dawson Khoury-Kobayashi | |
| 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 on page 2-24. The parameter requirements for the distinctive models are in the tables labeled Parameters Required for the BWR-LS Property Method on page 2-21, Parameters Required for the LK-PLOCK Property Method on page 2-22, Parameters Required for the PR-BM Property Method on page 2-23, and Parameters Required for the RKS-BM Property Method on page 2-24.

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

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

*Continued*

***Equation-of-State Property Methods for Hydrocarbons at High Pressure (continued)***

| 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 on page 2-21 and Parameters Required for Common Models on page 2-24 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. Aspen Plus 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<br>  Fugacity coefficient,<br>  Density<br>  Enthalpy, | BWR-Lee-Starling | TC, VC, OMEGA |
|   Entropy,<br>  Gibbs energy | Ideal heat capacity,<br>BWR-Lee-Starling | (CPIG or CPIGDP) and<br>TC, VC, OMEGA |
| Liquid mixture<br>  Fugacity coefficient,<br>  Density<br>  Enthalpy,<br>  Entropy, | BWR-Lee-Starling | TC, VC, OMEGA |
|   Gibbs energy | Ideal heat capacity,<br>BWR-Lee-Starling | (CPIG or CPIGDP) and<br>TC, VC, OMEGA |

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

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 on page 2-22 and Parameters Required for Common Models on page 2-24 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. ASPEN PLUS 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.

### *Parameters Required for the LK-PLOCK Property Method*

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| Vapor mixture<br>  Fugacity coefficient,<br>  Density | Lee-Kesler-Plöcker | TC, PC, VC, OMEGA |
| Enthalpy, entropy<br>Gibbs free energy | Ideal gas heat capacity,<br>Lee-Kesler-Plöcker | (CPIG or CPIGDP)<br>and TC, PC, VC, OMEGA |
| Liquid mixture<br>  Fugacity coefficient,<br>  Density | Lee-Kesler-Plöcker | TC, PC, VC, OMEGA |
| Enthalpy, entropy<br>Gibbs free energy | Ideal gas heat capacity,<br>Lee-Kesler-Plöcker | (CPIG or CPIGDP)<br>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 on page 2-23 and Parameters Required for Common Models on page 2-24 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. Aspen Plus does not have built-in binary parameters for this property method.

### Mixture Types

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

### Range

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

#### *Parameters Required for the PR-BM Property Method*

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| Vapor or liquid mixture<br>  Fugacity coefficient<br>  Density | Peng-Robinson | TCPR, PCPR, OMEGA |
| Enthalpy, entropy,<br>  Gibbs free energy | Ideal gas heat capacity,<br>Peng-Robinson | CPIG or CPIGDP,<br>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. Aspen Plus 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 and Parameters Required for Common Models on page 2-24 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<br>    Fugacity coefficient<br>    Density | Redlich-Kwong-Soave | TCRKS, PCRKS, OMGRKS |
|     Enthalpy, entropy,<br>    Gibbs free energy | Ideal gas heat capacity,<br>Redlich-Kwong-Soave | CPIG or CPIGDP,<br>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 on page 2-27 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 Plus 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 on page 2-35. Parameter requirements for the distinctive models are in the tables labeled Parameters Required for the PRMHV2 Property Method on page 2-28, Parameters Required for the PRWS Property Method on page 2-29, Parameters Required for the PSRK Property Method on page 2-30, Parameters Required for the RK-ASPEN Property Method on page 2-31, Parameters Required for the RKSMHV2 Property Method on page 2-32, Parameters Required for the RKSWS Property Method on page 2-33, and Parameters Required for the SR-POLAR Property Method on page 2-34.

### *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 | — |

| 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 |

[†]   *An X indicates volume shift is included in the property method.*

[††]   *An X indicates that the property method is predictive.*

# 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 on page 2-28 and Parameters Required for Common Flexible and Predictive Models on page 2-35. 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.

### *Parameters Required for the PRMHV2 Property Method*

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| Vapor and liquid mixture<br>  Fugacity coefficient,<br>  Density | Peng-Robinson-MHV2,<br>UNIFAC | TC, PC, OMEGA,<br>UFGRP, GMUFQ, GMUFR |
| Enthalpy,<br>Entropy,<br>Gibbs energy | Ideal heat capacity,<br>Peng-Robinson-MHV2,<br>UNIFAC | (CPIG or CPIGDP),<br>TC, PC, OMEGA,<br>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 on page 2-29 and Parameters Required for Common Flexible and Predictive Models on page 2-35. 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<br>  Fugacity coefficient,<br>  Density | Peng-Robinson-WS,<br>UNIFAC | TC, PC, OMEGA, UFGRP, GMUFR, GMUFQ |
| Enthalpy,<br>Entropy,<br>Gibbs energy | Ideal heat capacity, PengRobinson-WS,<br>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 on page 2-30 and Parameters Required for Flexible and Predictive Models on page 2-35. 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.

### *Parameters Required for the PSRK Property Method*

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| Vapor and liquid mixture<br>  Fugacity coefficient,<br>  Density | PSRK,<br>UNIFAC | TC, PC, OMEGA, UFGRP, GMUFR, GMUFQ |
| Enthalpy,<br>Entropy,<br>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 RKASPEN Property Method on page 2-31 and Parameters Required for Common Flexible and Predictive Models on page 2- 35. 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.

### *Parameters Required for the RK-ASPEN Property Method*

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| Vapor and liquid mixture<br>  Fugacity coefficient,<br>  Density | Redlich-Kwong-Aspen | TCRKA, PCRKA, OMEGARKA, UFGRP, GMUFR, GMUFQ |
| Enthalpy,<br>Entropy,<br>Gibbs energy | Ideal heat capacity,<br>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 on page 2-32 and Parameters Required for Common Flexible and Predictive Models on page 2-35. 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.

### *Parameters Required for the RKSMHV2 Property Method*

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| Vapor and liquid mixture<br>  Fugacity coefficient,<br>  Density | Redlich-Kwong-Soave-MHV2, Lyngby modified UNIFAC | TC, PC, OMEGA, UFGRPL, GMUFLR, GMUFLQ |
| Enthalpy,<br>Entropy,<br>Gibbs energy | Ideal heat capacity,<br>Redlich-Kwong-Soave-MHV2,<br>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 on page 2-33 and Parameters Required for Common Flexible and Predictive Models on page 2-35. 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.

### *Parameters Required for the RKSWS Property Method*

| 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, ASPEN PLUS 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 on page 2-34 and Parameters Required for Common Flexible and Predictive Models on page 2-35. 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<br>　Fugacity coefficient,<br>　Density | Schwartzentruber-Renon | TC, PC, OMEGA, Optional:<br>RKUPPn, RKUCn,<br>RKUKAn, RKULAn, RKUKBn<br>n = 0, 1, 2 |
| 　Enthalpy,<br>　Entropy,<br>　Gibbs energy | Ideal gas heat capacity/DIPPR<br>Schwartzentruber-Renon | (CPIG or CPIGDP)<br>Optional:<br>RKUPPn, RKUCn,<br>RKUKAn, RKULAn, RKUKBn<br>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 on page 2-37 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 Plus 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 on page 2-37 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 on page 2-51.

# 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

## *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<br>  Fugacity coefficient,<br>  Density | Redlich-Kwong | TC, PC |
| Enthalpy,<br>Entropy,<br>Gibbs energy | Ideal heat capacity,<br>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 ($b_i$, $p_i$ and $d_i$). If parameters are not available, Aspen Plus 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<br>  Fugacity coefficient,<br>  Density | Nothnagel | TB, TC, PC and (NTHA or NTHK) |
| Enthalpy,<br>Entropy,<br>Gibbs energy | Ideal heat capacity,<br>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<br>  Fugacity coefficient,<br>  Density | Hayden-O'Connell | TC, PC, RGYR, MUP, HOCETA |
| Enthalpy,<br>  Entropy,<br>  Gibbs energy | Ideal heat capacity,<br>Hayden-O'Connell | (CPIG or CPIGDP), TC, PC, RGYR, MUP, HOCETA |

## HF Equation of State

The only property method that has the HF equation of state as the vapor phase model is WILS-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 Plus Data Regression System (DRS), if necessary. For details about the model, see Chapter 3.

# 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*

| Property Method Name | Dataset Number | Binary Parameters | | | | | | Vapor Phase EOS Name | Poynting Correction |
|---|---|---|---|---|---|---|---|---|---|
| | | VLE Lit[†] | Reg[††] | LLE Lit[†] | Reg[††] | Henry Lit[†] | Reg[††] | | |
| 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 indicates the parameters were obtained from the literature.*

[††]  *An X 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 Plus databanks. For details, see Aspen Plus *Physical Property Data*, Chapter 1.

You can model the solubility of supercritical gases using Henry's law. Henry coefficients are available in the Aspen Plus databanks for many solutes with water and other solvents (see Aspen Plus *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 on page 2-42.

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<br>Fugacity coefficient,<br>Gibbs energy | NRTL liquid activity coefficient | NRTL |
| | Extended Antoine vapor pressure | PLXANT |
| | Henry's constant | Solvent: VC,<br>Solute-solvent: HENRY |
| | Brelvi-O'Connell | Solvent: TC, PC, (ZC or RKTZRA), Solute:<br>(VC or VLBROC) |
| Enthalpy,<br>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),<br>(ZC or RKTZRA) |

# UNIFAC

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

## *UNIFAC Property Methods*

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

[†]  *An X indicates the parameters were obtained from the literature.*
[††]  *An X indicates the parameters were regressed by AspenTech from experimental data in the Dortmund*
   *Databank (DDB).*

The original version of UNIFAC can predict VLE and LLE, using two sets of parameters. So there are two property methods based on the original UNIFAC model, one using the VLE datas et (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 Plus databanks for many solutes with water and other solvents (see Aspen Plus *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 on page 2-44).

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 on page 2-44).

The parameter sets for all UNIFAC models are regularly revised and extended. The table labeled UNIFAC Property Methods on page 2-44 gives the revision number currently used in Aspen Plus. 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, | UNIFAC | UFGRPD |
| Gibbs energy | 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 [†] Reg [††] | LLE Lit [†] Reg [††] | Henry Lit [†] Reg [††] | Vapor Phase EOS Name | Poynting Correction |
| UNIQUAC | 1 | X  X | X  X | X  X | Ideal Gas law | — |
| UNIQ-2 | 2 | X  X | X  X | X  X | Ideal Gas law | — |
| UNIQ-RK | 1 | —  X | —  — | X  X | Redlich-Kwong | X |
| UNIQ-HOC | 1 | —  X | —  — | X  X | Hayden-O'Connell | X |
| UNIQ-NTH | 1 | —  — | —  — | X  X | Nothnagel | X |

[†]  *An X indicates the parameters were obtained from the literature.*

[††]  *An X indicates the parameters were regressed by AspenTech from experimental data in the Dortmund Databank (DDB).*

The UNIQUAC model can describe strongly nonideal liquid solutions and liquid-liquid equilibria. The model requires binary parameters. Many binary parameters for VLE and LLE, from literature and from regression of experimental data, are included in the Aspen Plus databanks (for details, see Aspen Plus *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 Aspen Plus *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 on page 2-46).

Heats of mixing are calculated using the UNIQUAC model.

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

### Mixture Types

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

### Range

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

Parameter requirements for the UNIQUAC activity coefficient model are given in the following table. For details about the model, see 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) |

### Parameters Required for UNIQUAC Property Methods (continued)

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| 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

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

[†]  *An X indicates the parameters were obtained from the literature.*

[††]  *An X indicates the parameters were regressed by AspenTech from experimental data in the Dortmund Databank (DDB).*

The Van Laar model can describe nonideal liquid solutions with positive deviations from Raoult's law (see 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 Plus databank (see Aspen Plus *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  on page 2-48.

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 |

[†]    *An X indicates the parameters were obtained from the literature.*

[††]    *An X indicates the parameters were regressed by AspenTech from experimental data in the Dortmund Databank (DDB).*

The Wilson model can describe strongly nonideal liquid solutions. The model cannot handle two liquid phases. In that case use NRTL or UNIQUAC. The model requires binary parameters. Many binary parameters for VLE, from literature and from regression of experimental data, are included in the Aspen Plus databanks (for details, see Aspen Plus *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 Aspen Plus *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  on page 2-51.

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 on page 2-1 for more help.

For general thermodynamic principles, see Chapter 1. Chapter 5 contains specifics on electrolyte simulation. 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 on page 2-65. 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 only 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 simulation of sour water systems at limited concentration. For more accurate results, use the ELECNRTL property method.

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 |

**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-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 Plus databanks. See Aspen Plus *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 on page 2-65. 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 |

*Continued*

**Parameters Required for the ELECNRTL Property Method (continued)**

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| Enthalpy,<br>Entropy,<br>Gibbs energy | [Ideal gas heat capacity/<br>DIPPR/<br>Barin correlation<br>and<br>Redlich-Kwong | CPIG or<br>CPIGDP or<br>CPIXP1, CPIXP2, CPIXP3]<br><br>TC, PC |
| **Liquid mixture** | | |
| Fugacity coefficient,<br>Gibbs energy | Electrolyte NRTL | Mol.: CPDIEC<br>Ion: RADIUS<br>Mol.-Mol.: NRTL<br>Mol.-Ion, Ion-Ion: GMELCC, GMELCD<br>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.<br>solute: (VC or VLBROC) |
| Enthalpy,<br>Entropy | [Ideal gas heat capacity/<br>DIPPR<br>and<br>Watson/DIPPR heat of vaporization<br>or<br>[Infinite dilution heat capacity / Criss-Cobble<br>Electrolyte NRTL | CPIG or<br>CPIGDP<br><br>Solvent: TC, (DHVLWT or DHVLDP)]<br><br>Ions: CPAQ0 or<br>Ions: IONTYP, S025C ]<br>Mol.: CPDIEC<br>Ion: RADIUS<br>Mol.-Mol.: NRTL<br>Mol.-Ion, Ion-Ion: GMELCC, GMELCD<br>GMELCE, GMELCN |
| Density | Rackett/Clarke | Mol.: TC, PC, (VC or VCRKT), (ZC or<br>RKTZRA) Ion-ion: VLCLK |
| **Solid pure (and mixture)** | | |
| Enthalpy,<br>Entropy | Solids heat capacity polynomial/ Barin<br>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 Plus 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 on page 2-57. For general and transport property parameter requirements, see the table Parameters Required for General and Transport Property Models on page 2-65.

# 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.

### Range

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

For parameter requirements for the electrolyte NRTL model, see the table
labeled Parameters Required for the ELECNRTL Property Method on page 2-57.
For general and transport property parameter requirements, see the table
labeled Parameters Required for General and Transport Property Models on page
2-65.

# 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 Plus 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 on page 2-65. 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 and Redlich-Kwong | CPIG or CPIGDP or CPIXP1, CPIXP2, CPIXP3] TC, PC, OMEGA |
| Liquid mixture | | |
| Fugacity coefficient, Gibbs energy | Pitzer | Cation-anion: GMPTB0, GMPTB1, GMPTB2, GMPTB3, GMPTC <br> Cation-cation: GMPTTH <br> Anion-anion: GMPTTH <br> Cation1-cation2-common anion: GMPTPS <br> Anion1-anion2-common cation: GMPTPS <br> 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 Watson/DIPPR heat of vaporization or [Infinite dilution heat capacity / | CPIG or CPIGDP <br><br> Solvent: TC, (DHVLWT or DHVLDP)] <br><br> Ions: CPAQ0 or |
| | Criss-Cobble | Ions: IONTYP, S025C ] |
| | Pitzer | Cation-anion: GMPTB0,GMPTB1,GMPTB2,GMPTB3,GMPTC <br> Cation-cation: GMPTTH <br> Anion-anion: GMPTTH <br> Cation1-cation2-common anion: GMPTPS <br> Anion1-anion2-common cation: GMPTPS <br> Molecule-ion, Mol. – Mol.: GMPTB0,GMPTB1,GMPTC |

*Continued*

### Parameters Required for the PITZER Property Method (continued)

| Thermodynamic Properties | Models | Parameter Requirements |
|---|---|---|
| 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 Plus 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 on page 2-65. 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 Redlich-Kwong | CPIG or CPIGDP or CPIXP1, CPIXP2, CPIXP3] 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 Watson/DIPPR heat of vaporization or[Infinite dilution heat capacity / Criss-Cobble | CPIG or CPIGDP Solvent: TC, (DHVLWT or DHVLDP)] 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 on page 2-61, and the table labeled Parameters Required for General and Transport Property Models on page 2-65. 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<br>Solids,Salts: (DHSFRM or CPSXP1 to CPSXP7)<br>Ions: DHAQFM |
| Gibbs energy of reaction | Solvents, Mol. solutes: DGFORM<br>Solids,Salts: (DGSFRM or CPSXP1 to CPSXP7)<br>Ions: DGAQFM |

### 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 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 Aspen Plus *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 |
| 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) |

## Thermodynamic Properties (continued)

| Property | Models | Parameter Requirements |
|---|---|---|
| Liquid pure and mixture | | |
| Enthalpy, Entropy | [Ideal gas heat capacity/ DIPPR and Watson/DIPPR heat of vaporization | CPIG or CPIGDP  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 Plus.

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<br>STEAMNBS | ASME 1967<br>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. Aspen Plus 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

The STEAMNBS property method uses:

- 1984 NBS/NRC 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.

**Range**

Use the STEAMNBS property method for pure water and steam with temperature ranges of 273.15 K to 2000 K. The maximum pressure is over 10000 bar.

# 3 Property Model Descriptions

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

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, simulation 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 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 Plus 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 | Details |
|---|---|---|
| Thermodynamic Property Models | Equation-of-State Models<br>Activity Coefficient Models<br>Vapor Pressure and Liquid Fugacity Models<br>Heat of Vaporization Models<br>Molar Volume and Density Models<br>Heat Capacity Models<br>Solubility Correlations<br>Other | Thermodynamic Property Models |
| Transport Property Models | Viscosity Models<br>Thermal Conductivity Models<br>Diffusivity Models<br>Surface Tension Models | Transport Property Models |
| Nonconventional Solid Property Models | General Enthalpy and Density Models<br>Enthalpy and Density Models for Coal and Char | Nonconventional Solid Property Models |

# Pure Component Temperature-Dependent Properties

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

For example, Aspen Plus 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 |

*Continued*

### *Pure Component Temperature-Dependent Properties (continued)*

| Property | Submodel-Selection Parameter Element Number | Available Submodels | Default DIPPR Equation Number |
|---|---|---|---|
| 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, Aspen Plus 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, Aspen Plus 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, Aspen Plus will search for the parameters needed for the Aspen form of the equations.

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

If your simulation contains any temperature-dependent property parameters, (such as CPIGDP for DIPPR ideal gas heat capacity, entered on the Properties Parameters Pure Component form), Aspen Plus 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$^\blacklozenge$ |
|---|---|
| 100 | $Y = A + BT + CT^2 + DT^3 + ET^4$ |
| 101 | $Y = \exp[A + B/T + C\ln T + DT^E]$ |
| 102 | $Y = \left(AT^B\right)/\left(1 + C/T + D/T^2\right)$ |

*Continued*

### Available DIPPR Equations (continued)

| Equation Number | Equation Form♦ |
|---|---|
| 103 | $Y = A + B \exp - [C/TD]$ |
| 104 | $Y = A + B/T + C/T^3 + D/T^8 + E/T^9$ |
| 105 | $Y = A/B^{\left(1+(1-T/C)^D\right)}$ |
| 106 | $Y = A(1-Tr)^{\left(B+CTr+DTr^2+ETr^3\right)}$ |
| 107 | $Y = A + B[(C/T)/SINH(C/T)]^2 + D[(E/T)/COSH(E/T)]^2$ |
| 114[†, ††] | $Y = A^2/t + B - 2ACt - ADt^2 - \left(C^2t^3\right)/3 - \left(CDt^4\right)/2 - \left(D^2t^5\right)/5$ |
| 116[††, †††] | $Y = A^{0.35} + Bt^{(2/3)} + Ct^{(4/3)} + Dt + Et$ |

[†]      *Use only for liquid heat capacity*

[††]      $t = (1 - Tr)$

[†††]      *Use only for liquid density*

♦
|   |   |   |
|---|---|---|
| $Y$ | = | *Property value* |
| $T$ | = | *Temperature in Kelvins* |
| $A, B, C, D, E$ | = | *Coefficients (parameters)* |

This chapter 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, Entrophy, 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 Aspen Plus. The following tableprovides a list of available models, with corresponding Aspen Plus 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 Plus 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 |
| 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 |
| Standard Peng-Robinson | ESPRSTD0,ESPRSTD | V L | X | X |
| Standard Redlich-Kwong-Soave | ESRKSTD0,ESRKSTD | V L | X | X |
| 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 |

## Heat of Vaporization Models

| Property Model | Model Name | Phase(s) [†] | Pure [††] | Mixture [††] |
|---|---|---|---|---|
| Watson / DIPPR | 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 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 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 |

[†]  *V = Vapor; L = Liquid; S = Solid*

[††]  *An X indicates applicable to Pure or Mixture*

# Equation-of-State Models

**Aspen Plus 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 |
| 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 |

*Continued*

| Model | Type |
| --- | --- |
| 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 |
| Standard Peng-Robinson | Cubic |
| Standard Redlich-Kwong-Soave | Cubic |
| Wong-Sandler mixing rules | Mixing rules |

## ASME Steam Tables

The ASME steam tables (1967) are implemented like any other equation-of-state in Aspen Plus. 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 | $\gamma_i$ | OMEGA | X | -0.5 | 3.0 | — |
| BWRKV [†] | $\varepsilon_{ij}$ | 0 | X | -5.0 | 1.0 | — |
| BWRKT [†] | $\eta_{ij}$ | 0 | X | -5.0 | 1.0 | — |

[†]   *Binary interaction parameters BWRKV and BWRKT are available in Aspen Plus for a large number of components. (See Aspen Plus 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.

# 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

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

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

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

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

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

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

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

- 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 $\eta$ values are present in Aspen Plus.

## 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:

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

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 |
| $\varphi_i$ | = | True fugacity coefficient of component $i$ |
| $K_{ij}$ | = | Equilibrium constant for the dimerization of $i$ and $j$, on a pressure basis |
| | = | $-(B_{bound} + B_{metastable} + B_{chem})_{ij}(2-\delta_{ij})/RT$ |
| $\delta_{ij}$ | = | 1 for $i=j$ |
| | = | 0 for $i \neq j$ |

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:

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

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 $H_m^v - H_m^{ig}$.

| 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 | $r_i^{gyr}$ | — | — | $10^{-11}$ | $5 \times 10^{5-9}$ | LENGTH |
| MUP | $p_i$ | — | — | 0.0 | $5 \times 10^{5-24}$ | DIPOLEMOMENT |
| HOCETA [†] | $\eta$ | 0.0 | x | — | — | — |

[†]   ***The binary parameters HOCETA for many component pairs are available in Aspen Plus. 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 Simulation, 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:

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

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:

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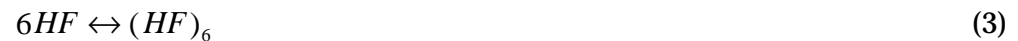
If $p_1$ represents the true partial pressure of the HF monomer, and $p_6$ represents the true partial pressure of the hexamer, then the equilibrium constant is defined as:

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

The true total pressure is:

$$p = p_1 + p_6 \tag{5}$$

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

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

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:

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

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.

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

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:

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

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

## Enthalpy and Entropy

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

$$v_A A + v_B B = v_C C + v_D D \tag{13}$$

$$RT \ln K = RT \ln \frac{p_{C^C}^v \, p_{D^D}^v}{p_{A^A}^v \, p_{B^B}^v} \tag{14}$$

Where $\mu_i^*$ 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:

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

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

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

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

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

$$G_m = H_m - TS_m \tag{18}$$

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 | — | — | — | — |

**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, "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 $\omega$, 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 |
| $\omega$ | OMGLK | OMEGA | Acentric factor |

### References

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.

$$p_c = Z_{cm}RT_c / V_{cm}$$

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:

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

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

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

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

The binary parameter $k_{ij}$ is determined from phase-equilibrium data regression, such as VLE data. Aspen Plus 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 | Upper Limit | Lower 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 |

*Continued*

| Parameter Name/Element | Symbol | Default | MDS | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| OMGLKP | $\omega_I$ | 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 [††] | $k_{ij}$ | $fcn\left(\frac{T_{ci}v_{ci}}{T_{cj}v_{cj}}\right)$ | 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 availablefor a large number of components in Aspen Plus.*

### 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 Aspen Plus. These steam tables can calculate any thermodynamic property of water. The tables form the basis of the STEAMNBS property method. There are no parameter requirements. They are the most accurate steam tables in Aspen Plus.

### 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:

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

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

$nc$  =  Number of components in the mixture

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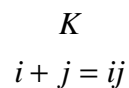
$$i + j \overset{K}{=} ij$$

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

$\varphi_i$    =    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 $\left(\dfrac{V}{n^t}\right)$ 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 Aspen Plus 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 | Upper Limit | Lower 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 | $b_i$ | $0.199RT_{ci}/p_{ci}$ | 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 Functionson page 3-40). 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 $\alpha_i$ 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 on page 3-40).

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 | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCPR | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PCPR | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| OMGPR | $\omega_i$ | 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 Aspen Plus.*

**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 on page 3-37, or in Peng-Robinson Alpha Functions on page 3-40.

The MHV2 mixing rules are an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules on page 3-49. 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 on page 3-38 and in Soave Alpha Functions on page 3-43.

The PSRK method is an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules on page 3-49. 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 on page 3-40.

The Wong-Sandler mixing rules are an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules on page 3-49. 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 | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TC | $T_{ci}$ | — | — | 5.0 | 2000.0 | TEMPERATURE |
| PC | $p_{ci}$ | — | — | $10^5$ | $10^8$ | 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 $a_i$ 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 | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCRKA | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PCRKA | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| OMGRKA | $\omega_i$ | OMEGA | x | -0.5 | 2.0 | — |
| RKAPOL | $\eta_i$ | 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. See the* Aspen Plus User Guide.

### 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 on page 3-43). 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:

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

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

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

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

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

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 on page 3-43).

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 | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCRKS | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PCRKS | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| OMGRKS | $\omega_i$ | 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 Aspen Plus.*

## 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 on page 3-38, and in Soave Alpha Functions on page 3-43.

The Wong-Sandler mixing rules are an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules on page 3-49. 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" on page 3-38, and in "Soave Alpha Functions" on page 3-43.

The MHV2 mixing rules are an example of modified Huron-Vidal mixing rules. A brief introduction is provided in Huron-Vidal Mixing Rules on page 3-49. 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:

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

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 | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCRKU | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PCRKU | $p_{ci}$ | PC | x | 105 | 108 | PRESSURE |
| OMGRKU | $\omega_i$ | 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 >> 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.*

### 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.

## 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 on page 3-40). 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 on page 40, equations 1 through 5).

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

| Parameter Name/Element | Symbol | Default | MDS | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCPRS | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PCPRS | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| OMGPRKSS | $\omega_i$ | 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 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:

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

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 according to the standard Soave formulation (see Soave Alpha Functions on page 3-43, 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). Aspen Plus 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 | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCRKSS | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PCRKSS | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| OMRKSS | $\omega_i$ | 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 Aspen Plus.*

### 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.

## 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 $\alpha$ 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 | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCPR | $T_{ci}$ | TC | X | 5.0 | 2000.0 | TEMPERATURE |
| PCPR | $p_{ci}$ | PC | X | $10^5$ | $10^8$ | PRESSURE |
| OMGPR | $\omega_i$ | 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 $\alpha$ 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

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

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

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.

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

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 | Upper Limit | Lower 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:

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

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:

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

$$c_i = 1 - \frac{1}{d_i} \tag{10}$$

| Parameter Name/Element | Symbol | Default | MDS | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCPR | $T_{ci}$ | TC | X | 5.0 | 2000.0 | TEMPERATURE |
| PCPR | $p_{ci}$ | PC | X | $10^5$ | $10^8$ | PRESSURE |
| OMGPR | $\omega_i$ | 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<br>ESPRWS0, ESPRWS<br>ESPRV20, ESPRV2 | —<br>1<br>1 |
| Mathias-Copeman | ESPRWS0, ESPRWS<br>ESPRV20, ESPRV2 | 2<br>2 |
| Schwartzentruber-Renon-Watanasiri | ESPRWS0, ESPRWS<br>ESPRV20, ESPRV2 | 3 (default)<br>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:

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

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

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

## Soave Modification

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

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

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 | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCRKS | $T_{ci}$ | TC | X | 5.0 | 2000.0 | TEMPERATURE |
| PCRKS | $p_{ci}$ | PC | X | $10^5$ | $10^8$ | PRESSURE |
| OMGRKS | $\omega_i$ | 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 $\alpha$ reduces asymptotically to zero. Boston and Mathias derived an alternative function for temperatures higher than critical:

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

(7)

With

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

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

Where:

$$m_i \qquad = \quad \text{Computed by equation 6}$$

$$\text{Equation 5} \quad = \quad \text{Used for subcritical temperatures}$$

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:

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

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:

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

(9)

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

(10)

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

### Extended Mathias Alpha Function

An extension of the Mathias approach is:

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

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:

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

$$c_i = 1 - \frac{1}{d_i} \tag{13}$$

| Parameter Name/Element | Symbol | Default | MDS | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCRKU | $T_{ci}$ | TC | X | 5.0 | 2000.0 | TEMPERATURE |
| PCRKU | $p_{ci}$ | PC | X | $10^5$ | $10^8$ | PRESSURE |
| OMGRKU | $\omega_i$ | 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:

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

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 | Upper Limit | Lower 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:

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

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:

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

$$c_i = 1 - \frac{1}{d_i} \tag{17}$$

| Parameter Name/Element | Symbol | Default | MDS | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TCPR | $T_{ci}$ | TC | X | 5.0 | 2000.0 | TEMPERATURE |
| PCPR | $p_{ci}$ | PC | X | $10^5$ | $10^8$ | PRESSURE |
| OMGPR | $\omega_i$ | 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<br>ESRKSWS0, ESRKSWS<br>ESRKSV10, ESRKV1<br>ESRKSV20, ESRKSV2 | —<br>1<br>1<br>1 |
| Mathias/Boston-Mathias | ESRKA0, ESRKA | — |
| Extended Mathias/Boston-Mathias | ESRKU0, ESRKU | — |
| Mathias-Copeman | ESRKSW0, ESRKSW<br>ESRKSV10, ESRKSV1<br>ESRKSV20, ESRKSV2 | 2<br>2<br>2 |
| Schwartzentruber-Renon-Watanasiri | ESPRWS0, ESPRWS<br>ESRKSV10, ESRKSV1<br>ESRKSV20, ESRKSV2 | 3 (default)<br>3 (default)<br>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:

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

Where:

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

The parameters $\lambda_1$ and $\lambda_2$ depend on the equation-of-state used. In general a cubic equation-of-state can be written as:

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

Values for $\lambda_1$ and $\lambda_2$ for the Peng-Robinson and the Soave-Redlich-Kwong equations of state are:

| Equation-of-state | $\lambda_1$ | $\lambda_2$ |
|---|---|---|
| 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 Plus 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.

### References

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 $\alpha$:

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

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 $\lambda_1$ and $\lambda_2$, 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 $\alpha$ 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 $\alpha$, if $\alpha_i$, $b_i$, 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) on page 3-75). 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).

### References

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:

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

With:

$$b = \sum_i x_i b_i$$
(4)

Therefore:

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

The mixing rule is:

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

Where $\Lambda'$ is slightly different from $\Lambda$ for the Huron-Vidal mixing rule:

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

Where $\lambda_1$ and $\lambda_2$, 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:

$$A_m^{E,l}(p) = G_m^{E,l}(p = 1atm) + \int_{V_m^l = 1.1b}^{V_m^l = b} p\, dV_m^l - \sum_i x_i \int_{V_i^{*,l} = 1.1b}^{V_i^{*,l} = b} p\, dV_i^{*,l}$$
(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 Aspen Plus 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.

### References

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:

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

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

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

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.

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 $\Lambda$ 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

Aspen Plus 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 |

| Model | Type |
|-------|------|
| 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 Aspen Plus 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 $\theta$ 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 | $\beta_{ion}$ | 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-IonParameters | | | | |
| 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 coefficient 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

Aspen Plus 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, $\alpha$, and energy parameters, $\tau$. 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:

$T^{ref}$    =    298.15K

Many parameter pairs are included in the electrolyte NRTL model parameter databank (see *Aspen Plus 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** | | | | | |
| Parameter Name | Symbol | No. of Elements | Default | MDS | Units |
| RADIUS | $r_i$ | 1 | 3x10-10 | — | 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 | — |

| Parameter Name | Symbol | No. of Elements | Default | MDS | Units |
|---|---|---|---|---|---|
| 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 | — |
|  | $\alpha_{c'a,c''a} = \alpha_{c''a,c}$ | 1 | .2 | x | — |

[†]    *If dielectric constant parameters are missing for a solvent, the dielectric constant of water is automatically assigned.*

[††]    *Absolute temperature units are assumed (Aspen Plus User Guide, Chapter 8, Volume 1).*

[†††]  *If an electrolyte-molecule parameter is missing, the following defaults are used:*

| | |
|---|---|
| *Electrolyte-water* | *-4* |
| *Water-electrolyte* | *8* |
| *Electolyte-solvent* | *-2* |
| *Solvent-electrolyte* | *10* |
| *Electrolyte-solute* | *-2* |
| *Solute-electrolyte* | *10* |

## 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:

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

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

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

$$\tau_{ii} = 0$$

$$G_{ii} = 1$$

$$a_{ij} \neq a_{ji}$$

$$b_{ij} \neq b_{ji}$$

$$c_{ij} \neq c_{ji}$$

$$d_{ij} \neq d_{ji}$$

### 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. Aspen Plus 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 *Aspen Plus Physical Property Data*, Chapter 1 for details.

| Parameter Name/Element | Symbol | Default | MDS | Upper Limit | Lower 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 |

† *Absolute temperature units are assumed.*

### 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 Aspen Plus 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 $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$, $c^{\varphi}$, and $\theta$. 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 Aspen Plus (see *Aspen Plus Physical Property Data*, Chapter 1).

| 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 | $C^{\theta}$ | 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 | $C^{\theta}$ | 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:

$$A_i \;=\; a_{i1}/T + a_{i2} + a_{i3} \ln(T)$$

$$B_i \;=\; b_{i1}/T + b_{i2} + b_{i3} \ln(T)$$

$$C_i \;=\; c_{i1}/T + c_{i2} + c_{i3} \ln(T)$$

$$D_i \;=\; d_{i1}/T + d_{i2} + d_{i3} \ln(T)$$

$$E_i \;=\; e_{i1}/T + e_{i2} + e_{i3} \ln(T)$$

For any component i, the value of the activity coefficient can be fixed:

$$\gamma_i = f_i$$

| Parameter Name/Element | Symbol | Default | MDS | Upper Limit | Lower 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:

$$\ln \gamma_i = \sum_{j=1}^{nc} \left[ \sum_{n=1}^{5} x_j A_{n,ij} \left( x_i - x_j \right)^{(n-2)} \left( nx_i - x_j \right) - \frac{1}{2} \sum_{k=1}^{nc} \sum_{n=1}^{5} x_j x_k A_{n,jk} \left( x_j - x_k \right)^{(n-2)} \left[ (2n-1)x_j - x_k \right. \right.$$

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 | Upper Limit | Lower 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 | — | — | — |

| Parameter Name/ Element | Symbol | Default | MDS | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| 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:

$$A_{ij} \quad = \quad 2\left(\delta_i - \delta_j\right)^2$$

$$\varphi_i \quad = \quad \frac{x_i V_i^{*,l}}{V_m^l}$$

$$V_m^{*,L} \quad = \quad \sum_i x_i V_i^{*,l}$$

The Scatchard-Hildebrand model does not require binary parameters.

| Parameter Name/Element | Symbol | Default | MDS | Upper Limit | Lower Limit | Units |
|---|---|---|---|---|---|---|
| TC | $T_{ci}$ | — | x | 5.0 | 2000.0 | TEMPERATURE |
| DELTA | $\delta_i$ | — | x | $10^3$ | $10^5$ | SOLUPARAM |
| VLCVT1 | $V_i^{*,CVT}$ | — | x | 0.0005 | 1.0 | MOLE-VOLUME |
| GMSHVL | $V_i^{*,I}$ | $V_i^{*,I} = V_i^{*,CVT}$ $5.7 + 3.0\left(\frac{298.15}{T_{ci}}\right)$ | 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:

$$\ln \gamma_i = \tfrac{1}{2} \sum_j^{nc} \left( k_{ij} + k_{ji} \right) x_j - \sum_j^{nc} \sum_l^{nc} k_{jl} x_j x_l + \sum_j^{nc} \left( k_{ij} - k_{jl} \right) x_j \left( x_j/2 - x_i \right) \sum_j^{nc} \sum_l^{nc} \left( k_{jl} - k_{ljj} \right) x_l x_j^2$$

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 | Upper Limit | Lower 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, 2<sup>nd</sup> 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, 4<sup>th</sup> 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 Aspen Plus.

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:

$$\Phi_i = \frac{x_i r_i}{\sum_j^{nc} x_j r_j} \text{ and } \theta_i = \frac{x_i \frac{z}{2} q_i}{\sum_j^{nc} x_j \frac{z}{2} q_j}$$

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:

$$r_i = \sum_k^{ng} v_{ki} R_k \text{ and } q_i = \sum_k^{ng} v_{ki} Q_k$$

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:

$$\ln \gamma_i^r = \sum_k^{ng} v_{ki}\left[\ln \Gamma_k - \ln \Gamma_k^i\right]$$

$\Gamma_k$ is the activity coefficient of a group at mixture composition, and $\Gamma_k^i$ is the activity coefficient of group $k$ in a mixture of groups corresponding to pure $i$. The parameters $\Gamma_k$ and $\Gamma_k^i$ 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 | SymbolT | 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 Plus pure component databank for most components. For nondatabank components, enter UFGRP on the Properties Molecular Structure Functional Group sheet. See *Aspen Plus Physical Property Data*, Chapter 3, for a list of the UNIFAC functional groups.

### References

Aa. Fredenslund, R.L. Jones and J.M. Prausnitz, AIChE J., Vol. 21, (1975), p. 1086.

Aa. Fredenslund, J. Gmehling and P. Rasmussen, "Vapor-Liquid Equilibria using UNIFAC," (Amsterdam: Elsevier, 1977).

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 | SymbolT | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| UFGRPD | $\left(k\nu_{ki}\, m\nu_{mi}\,...\right)$ | — | — | — | — | — |
| GMUFDQ | $Q_k$ | — | — | — | — | — |
| GMUFDR | $R_k$ | — | — | — | — | — |
| UNIFDM/1 | $a_{mn,1}$ | 0 | — | — | — | TEMPERATURE |
| UINFDM/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 Plus pure component databank. For nondatabank components, enter UFGRPD on the Properties Molecular Structure Functional Group sheet. See *Aspen Plus Physical Property Data*, Chapter 3, for a list of the Dortmund modified UNIFAC functional groups.

### References

U. Weidlich and J. Gmehling, "A Modified UNIFAC Model 1. Prediction of VLE, $h^E$ and $\gamma^\infty$," 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 $\Gamma_k$ and $\Gamma_k^i$ 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:

$$\theta_k = \frac{X_k \dfrac{z}{2} Q_k}{\sum_m^{ng} X_m \dfrac{z}{2} Q_m}$$

$$\tau_{mn} = e^{-a_{mn}/T}$$

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 T | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| UFGRPL | $(\nu_{ki} \ \nu_{mi} \dots)$ | — | — | — | — | — |
| GMUFLQ | $Q_k$ | — | — | — | — | — |
| GMUFLR | $R_k$ | — | — | — | — | — |

| Parameter Name/Element | Symbol T | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| 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 Plus pure component databank. For nondatabank components, enter UFGRP on the Properties Molec-Struct.Func Group form. See *Aspen Plus Physical Property Data*, Chapter 3, for a list of the Larsen modified UNIFAC functional groups.

### References

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:

$$\theta_i \ = \ q_i x_i \bigg/ q_T \ ; \ q_T = \sum_k q_k x_k$$

$$\theta_i' \ = \ q_i' x_i \bigg/ q_T' \ ; \ q_T' = \sum_k q_k' x_k$$

$$\Phi_i = \quad \Phi_i = r_i x_i \bigg/ r_T \ ; \ r_T = \sum_k r_k x_k$$

$$l_i = \frac{z}{2}(r_i - q_i) + 1 - r_i$$

$$t_i' = \sum_k \theta_k' \tau_{ki}$$

$$\tau_{ij} = \exp(a_{ij} + b_{ij}/T + C_{ij}\ln T + d_{ij}T$$

$$z = 10$$

$$a_{ij} \neq a_{ji}$$

$$b_{ij} \neq b_{ji}$$

$$c_{ij} \neq c_{ji}$$

$$d_{ij} \neq d_{ji}$$

The binary parameters $a_{ij}$, $b_{ij}$, $c_{ij}$, and $d_{ij}$ can be determined from VLE and/or LLE data regression. Aspen Plus 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 Chapter 1, *Aspen Plus Physical Property Data*, 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.

$$\ln \gamma_i = A_i\left(1 - z_i\right)^2 \left[1 + C_i z_i (z_i - \tfrac{2}{3}) + 2 z_i \left(A_i B_i / |A_i B_i| - 1\right)\right]$$

Where:

$$z_i = \frac{|A_i| x_i}{|A_i| x_i + |B_i|\left(1 - x_i\right)}$$

$$A_i = \sum_j x_j A_{ij} / \left(1 - x_i\right)$$

$$B_i = \sum_j x_j A_{ji} / \left(1 - x_i\right)$$

$$C_i = \sum_j x_j C_{ij} / (1 - x_i)$$

$$A_{ij} = a_{ij} + b_{ij} / T$$

$$C_{ij} = c_{ij} + d_{ij} / T$$

$$C_{ij} = C_{ji}$$

$$A_{ii} = B_{ii} = C_{ii} = 0$$

$$a_{ij} \neq a_{ji}$$

$$b_{ij} \neq b_{ji}$$

| 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 [†] |

[†]    *Absolute temperature units are assumed.*

### 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 $\gamma_i^{ref}$ 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:

$$\ln A_{ij} \quad = \quad a_{ij} + b_{ij}/T + c_{ij} \ln T + d_{ij} T$$

$$a_{ij} \neq a_{ji}$$

$$b_{ij} \neq b_{ji}$$

$$c_{ij} \neq c_{ji}$$

$$d_{ij} \neq d_{ji}$$

The binary parameters $a_{ij}$, $b_{ij}$, $c_{ij}$, and $d_{ij}$ must be determined from VLE data regression. Aspen Plus 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 Chapter 1, *Aspen Plus Physical Property Data*, 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:

$$\ln A_{ij} \quad = \quad \ln \frac{V_j}{V_i} + \frac{b_{ij}}{T}$$

$$b_{ij} \quad \neq \quad b_{ji}$$

$V_i$ 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.

### References

G.M. Wilson, *J. Am. Chem. Soc.,* Vol. 86, (1964), p. 127.

# Vapor Pressure and Liquid Fugacity Models

Aspen Plus 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 |

## 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 Plus pure component databank. This equation is used whenever the parameter PLXANT is available.

The equation for the extended Antoine vapor pressure model is:

$$\ln p_i^{*,l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln T + C_{6i}t^{C_{7i}} \; for \; C_{8i} \leq C_{9i}$$

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 | $C_{3i}, \ldots, C_{7i}$ | 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:

$$\ln p_{ri}^{*,l} = \left[ C_{1i}(1 - T_{ri}) + C_{2i}(1 - T_{ri})^{1.5} + C_{3i}(1 - T_{ri})^3 + C_{4i}(1 - T_{ri})^4 \right] \Big/ T_{ri}$$

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 |

### 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.

### IK-CAPE Vapor Pressure Equation

The IK-CAPE model is a polynomial equation. If the parameter PLPO is available, Aspen Plus 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 | $C_{2i}, ..., C_{10i}$ | 0 | X | — | — | TEMPERATURE |
| PLPO/11 | $C_{11i}$ | 0 | X | — | — | TEMPERATURE |
| PLPO/12 | $C_{12i}$ | 1000 | X | — | — | TEMPERATURE |

## 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:

$$\nu_i^{(0)}, \nu_i^{(1)} \quad = \quad fcn(T, T_{ci}, p, p_{ci})$$

| 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 |
| OMEGA | $\omega_i$ | — | — | -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 property method. 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:

$$\nu_i^{(0)}, \nu_i^{(1)} = fcn(T, T_{ci}, p, p_{ci})$$

| 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 |
| OMEGA | $\omega_i$ | — | — | -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:

$$RR'NH_2^+ \overset{K_1}{=} H^+ + RR'NH$$

$$RR'NCOO^- + H_2O \overset{K_2}{=} RR'NH + HCO_3^-$$

$$H_2O + CO_2 \overset{K_3}{=} H^+ + HCO_3^-$$

$$H_2O \overset{K_4}{=} H^+ + OH^-$$

$$HCO_3^- \overset{K_5}{=} H^+ + CO_3^{2-}$$

$$H_2S \overset{K_6}{=} H^+ + HS^{2-}$$

$$HS^- \overset{K_7}{=} H^+ + S^{2-}$$
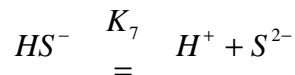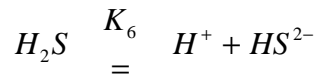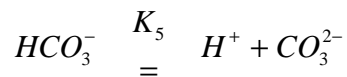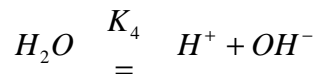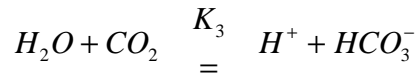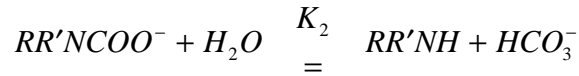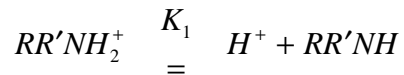
Where:

$R$ and $R'$ = 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 Aspen Plus. 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.

# Heat of Vaporization Model

Aspen Plus 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 | $C_{2i},\ldots,C_{5i}$ | 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:

$$\Delta_{vap} H_i^*(T) = \Delta_{vap} H_i^*(T_1)\left(\frac{1-T/T_{ci}}{1-T_1/T_{ci}}\right)^{a_i+b_i\left(1-1-T/T_{ci}\right)} \quad for\, T > T_{min}$$

Where:

$\Delta_{vap} H_i^* (T_1)$ = Heat of vaporization at temperature $T_1$

| Parameter Name/Element | Symbol | Default | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|
| TC | $T_{ci}$ | — | 5.0 | 2000.0 | TEMPERATURE |
| DHVLWT/1 | $\Delta_{vap} H_i^* (T_1)$ | — | $5X10^4$ | $5X10^8$ | 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 | $C_{2i},…,C_{10i}$ | 0 | X | — | — | MOLE-ENTHALPY TEMPERATURE |
| DHVLPO/11 | $C_{11i}$ | 0 | X | — | — | TEMPERATURE |
| DHVLPO/12 | $C_{12i}$ | 1000 | X | — | — | TEMPERATURE |

## Clausius-Clapeyron Equation

Aspen Plus 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

Aspen Plus 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:

$$V_p^l = fcn(T, T_b, API)$$

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:

$$V_r^l = \frac{RT_c Z^{RA\left[1+(1-T_r)^{2/7}\right]}}{p_c}$$

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 on page 3-110.) 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 Simulation, 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:

$$V^{\infty}_{CaCl_2} + V^{\infty}_{Na_2SO_4} = V^{\infty}_{CaSO_4} + 2V^{\infty}_{NaCl}$$

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:

$$V^{l,t}_m = V^{l,a}_m \frac{n^a}{n^t}$$

Where:

| | | |
|---|---|---|
| $V^{l,t}_m$ | = | Liquid volume per number of true species |
| $V^{l,a}_m$ | = | Liquid volume per number of apparent species, $V^l_m$ 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:

$$V^l_m(T) = V^l_m(298K)\frac{\sum_B x_B V^{*,l}_B(T)}{\sum_B x_B V^{*,l}_B(298K)}$$

Where:

| | | |
|---|---|---|
| $B$ | = | Any solvent |

| Parameter Name/Element | Applicable Components | Symbol | Default | Units |
|---|---|---|---|---|
| VLCLK/1 | Cation-Anion | $V^{\infty}_{ca}$ | † | 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 $V_m^{R,5}$ 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:

$$V_m^{CTD} = \tfrac{1}{4}\left[\left(\sum_i x_i V_i^{*,CTD} + 3\sum x_i V_i^{*.CTD}\right)^{2/3}\left(\sum_I x_i V_i^{*,CTD}\right)^{1/3}\right]$$

$$V_m^{CTD}T_c = \sum_i \sum_j x_i x_j V_{ij}^{CTD}T_{cij}$$

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

Where:

$$V_{ij}^{CTD}T_{cij} = \left(V_i^{*,CTD}T_{ci}V_j^{*,CTD}T_{cj}\right)^{1/2}$$

| 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 | $\omega_i$ | 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:

$V_k^\infty$ 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.

$$V_k = V_k^\infty + |z_k| 10^{-3} \left( \frac{A_V}{3b} \right) \ln\left(1 + bI^{1/2}\right)$$

Where:

| | | |
|---|---|---|
| $V_k^\infty$ | = | 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:

| | | |
|---|---|---|
| $A_\varphi$ | = | Debije-Hückel constant for the osmotic coefficients (Pitzer, 1979) |

$$\frac{1}{3} \left( 2\pi \left(10^{-3} \rho_w \right) N_A \right)^{1/2} \left( \frac{Q_e^2}{\varepsilon_w k_B T} \right)^{3/2}$$

$\rho_w$      =    Density of water $(\text{kg} / \text{m}^{-3})$

$\varepsilon_w$      =    Dielectric constant of water $(\text{Fm}^{-1})$, a function of pressure and temperature (Bradley and Pitzer, 1979)

| Parameter Name | Applicable Components | Symbol | Default | Units |
|---|---|---|---|---|
| VLBROC | Ions, molecular Solutes | $V_k^\infty$ | 0 | MOLE-VOLUME |

### References

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).

## 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.)*

### IK-CAPE

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 | $C_{2i},...,C_{10i}$ | 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:

$$V_i^{*,l} = \frac{RT_{ci}\left(Z_i^{*,RA}{}^{\left[1+\left(1-T_r\right)^{2/7}\right]}\right)}{p_{ci}}$$

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 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 on page 3-92.)

The equation for the Rackett model is:

$$V_m^l = \frac{RT_c \left( Z_m^{RA} \right)^{\left[ 1 + (1 - T_r)^{2/7} \right]}}{P_c}$$

Where:

$$T_c \quad = \quad \sum_i \sum_j x_i x_j V_{ci} V_{cj} \left( T_{ci} T_{cj} \right)^{1/2} \left( 1 - k_{ij} \right) \bigg/ V_{cm}^2$$

$$\frac{T_c}{P_c} \quad = \quad \sum_i x_i \frac{T_{ci}}{P_{ci}}$$

$$Z_m^{RA} \quad = \quad \sum_i x_i Z_i^{*,RA}$$

$$V_{cm} \quad = \quad \sum_i x_i V_{ci}$$

$$T_r \quad = \quad \frac{T}{T_c}$$

| 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 | $V_{ci}$ | ZC | x | 0.1 | 1.0 | — |
| RKTKIJ | $k_{ij}$ | $1 - \dfrac{8\left(V_{ci} V_{cj}\right)^{\frac{1}{2}}}{\left(V_{ci}^{\frac{1}{3}} + V_{cj}^{\frac{1}{3}}\right)^3}$ | x | -5.0 | 5.0 | — |

### 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.

## 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:

$$V_m^l = \frac{R T_c \left(Z_m^{RA}\right)^{\left[1 + \left(1 - T_r\right)^{\frac{2}{7}}\right]}}{P_c}$$

Where:

$$T_c = \sum_i \sum_j x_i x_j V_{ci} V_{cj} \left(T_{ci} T_{cj}\right)^{1/2} \left(1 - k_{ij}\right) \Big/ V_{cm}^2$$

$$k_{ij} = A_{ij} + B_{ij}T + C_{ij}T^2$$

$$\frac{T_c}{P_c} = \sum_i x_i \frac{T_{ci}}{P_{ci}}$$

$$Z_m^{RA} = \sum_i x_i Z_i^{*,RA}$$

$$V_{cm} = \sum_i x_i V_{ci}$$

$$T_r = \frac{T}{T_c}$$

| 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 | $A_{ij}$ | 0 | 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.

| Aspen Plus 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:

$$V_i^{*,s} = C_{1i} + C_2T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 \text{ for } C_{6i} \leq T \leq C_{7i}$$

| Parameter Name | Applicable Components | Symbol | MDS | Default | Units |
|---|---|---|---|---|---|
| VSPOLY/1 | Salts, CI solids | $C_{1i}$ | x | — | † |
| VSPOLY/2, . . . , 5 | Salts, CI solids | $C_{2i}, \ldots, C_{5i}$ | x | 0 | † |
| VSPOLY/6 | Salts, CI solids | $C_{6i}$ | x | 0 | † |
| VSPOLY/7 | Salts, CI solids | $C_{7i}$ | x | 1000 | † |

†    *The units are TEMPERATURE and MOLE-VOLUME.*

## IK-CAPE Equation

The IK-CAPE equation is a polynomial equation containing 10 terms. If the parameter VSPO is available, Aspen Plus 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 | $C_{2i}, \ldots, C_{10i}$ | 0 | X | — | — | MOLE-VOLUME TEMPERATURE |
| VSPO/11 | $C_{11i}$ | 0 | X | — | — | TEMPERATURE |
| VSPO/12 | $C_{12i}$ | 1000 | X | — | — | TEMPERATURE |

# Heat Capacity Models

Aspen Plus 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:

$$C_{p,i}^{\infty,aq} = C_1 + C_2 T + C_{3i} T^2 + \frac{C_{4i}}{T} + \frac{C_{5i}}{T^2} + \frac{C_{6i}}{\sqrt{T}} \text{ for } C_{7i} \leq T \leq C_{8i}$$

$C_{p,i}^{\infty,aq}$ 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 | Units |
| --- | --- | --- | --- | --- |
| 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 |

[†]   $IONTYP$ = 1 for cations
   = 2 for simple anions and hydroxide ions
   = 3 for oxy anions
   = 4 for acid oxy anions
   = 5 for hydrogen ion

## 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):

$$H_i^{*,l}(T) - H_i^{*,l}\left(T^{ref}\right) = \int_{T^{ref}}^{T} C_{p,i}^{*,l}\, dT$$

$H_i^{*,l}\left(T^{ref}\right)$ is calculated as:

$$H_i^{*,l}\left(T^{ref}\right) = H_i^{*,ig} + \left(H_i^{*,v} - H_i^{*,ig}\right) - \Delta_{vap} H_i^{*,l}$$

$T^{ref}$ 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 | Aspen Plus 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[†] | — | — | — | — | — | TEMPERATURE |

[†] *To specify that the model is used for a component, enter a value of 1.0 for this component parameter.*

## 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 | $C_{1i}$ | —<br>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 Plus 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 Ali and Lee 1981 is:

$$C_p^{*,ig} = C_{1i} + C_{2i}\left(\frac{C_{3i}/T}{\sinh\left(C_{3i}/T\right)}\right)^2 + C_{4i}\left(\frac{C_{5i}/T}{\cosh\left(C_{5i}/T\right)}\right)^2 \text{ for } C_{6i} \le T_{7i} \le C_{8i}$$

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 |
|---|---|---|---|---|---|---|
| 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 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.

$$C_p^{*,ig} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 \text{ for } C_{6i} \leq T \leq C_{7i}$$

$$C_p^{*,ig} = C_{9i} + C_{10i}T^{C_{11i}} \text{ for } T < C_{7i}$$

$C_p^{*,ig}$ 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 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).

Aspen Plus 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 | Units |
|---|---|---|---|---|---|
| CPSPO1/1 | Solids, Salts | $C_{1i}$ | x | — | [††] |
| CPSPO1/2, . . . , 6 | Solids, Salts | $C_{2i}, \ldots, C_{6i}$ | 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 | $C_{2i},...,C_{10i}$ | 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

Aspen Plus 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:

$$w_A = \frac{x_A (V_{cA})^{2/3}}{\sum_B x_B (V_{cB})^{2/3}}$$

$$\ln H_{iA}(T, p_A^{*,l}) = a_{iA} + b_{iA}/T + c_{iA} \ln T + d_{iA}T \text{ for } T_L \leq T \leq T_H$$

$$H_{iA}(T, P) = H_{iA}(T, p_A^{*,l}) \exp\left( \frac{1}{RT} \int_{p_a^{*,l}}^{p} V_{iA}^{\infty} dp \right)$$

The parameter $V_{iA}^{\infty}$ is obtained from the Brelvi-O'Connell model. $p_A^{*,l}$ is obtained from the Antoine model. $\gamma^{\infty}$ 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. Aspen Plus 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 *Aspen Plus 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 Plus 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*

# Other Thermodynamic Property Models

Aspen Plus 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 Plus inorganic databank are retrieved.

- **Gibbs energy:**

$$G_i^{*,\alpha} = a_{n,i}^{\alpha} + b_{n,i}^{\alpha} T + c_{n,i}^{\alpha}\left(T \ln T\right) + d_{n,i}^{\alpha} T^2 + e_{n,i}^{\alpha} T^3 + f_{n,i}^{\alpha} T^4 + g_{n,i}^{\alpha} T^{-1} + h_{n,i}^{\alpha} T^{-2} \tag{1}$$

- **Enthalpy:**

$$H_i^{*,\alpha} = a_{n,i}^{\alpha} - c_{n,i}^{\alpha} T - d_{n,i}^{\alpha} T^2 - 2 e_{n,i}^{\alpha} T^3 - 3 f_{n,i}^{\alpha} T^4 + 2 g_{n,i}^{\alpha} T^{-1} + 3 h_{n,i}^{\alpha} T^{-2} \tag{2}$$

- **Entropy:**

$$S_i^{*,\alpha} = -b_{n,i}^{\alpha} - c_{n,i}^{\alpha}\left(1 + \ln T\right) - 2 d_{n,i}^{\alpha} T - 3 e_{n,i}^{\alpha} T^2 - 4 f_{n,i}^{\alpha} T^3 + g_{n,i}^{\alpha} T^{-2} + 2 h_{n,i}^{\alpha} T^{-3} \tag{3}$$

- **Heat capacity:**

$$C_{p,i}^{*,\alpha} = -c_{n,i}^{\alpha} - 2 d_{n,i}^{\alpha} T - 6 e_{n,i}^{\alpha} T^2 - 12 f_{n,i}^{\alpha} T^3 - 2 g_{n,i}^{\alpha} T^{-2} - 6 h_{n,i}^{\alpha} T^{-3} \tag{4}$$

$\alpha$ 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:

$$H_i^{*,\alpha}(T) - H_i^{*,\alpha}(T^{ref}) = \int_{T^{ref}}^{T} C_{p,i}^{*,\alpha} dT$$

$$S_i^{*,\alpha}(T) - S_i^{*,\alpha}(T^{ref}) = \int_{T^{ref}}^{T} \frac{C_{p,i}^{*,\alpha}}{T} dT$$

$$G_i^{*,\alpha} = H_i^{*,\alpha} - TS_i^{*,\alpha}$$

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 | — | — | †† |

*Continued*

| Parameter Name[†]/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| 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 $H_k^\infty$ 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-EHTHALPY |
|  | Water | $\Delta_f H_w^{*,ig}$ | — | MOLE-ENTHALPY |
| CPIG | Molecular Solutes | $C_{p,i}^{*,ig}$ | — | [†††] |
|  | Water | $C_{p,w}^{*,ig}$ | — | [†††] |

[†]   *Not needed if CPAQ0 is given for ions*

[††]   *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. (See* Aspen Plus User Guide.*)*

## 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) $\mu_w^*$ 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 $\mu_k^\infty$ 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 | $C_{p,i}^{*,ig}$ | — | [†††] |
| | Water | $C_{p,w}^{*,ig}$ | — | [†††] |

[†]  *Not needed if CPAQ0 is given for ions*

[††]  *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. (See* Aspen Plus User Guide*.)*

## Liquid Enthalpy from Liquid Heat Capacity Correlation

Liquid enthalpy is directly calculated by integration of liquid heat capacity:

$$H_i^{*,l}(T) = H_i^{*,l}\left(T^{ref}\right) + \int_{T^{ref}}^{T} C_{p,i}^{*,l} dT$$

The reference enthalpy is calculated at $T^{ref}$ as:

$$H_i^{*,l}\left(T^{ref}\right) = H_i^{*,ig} + \left(H_i^{*,v} - H_i^{*,ig}\right) - \Delta_{vap} H_i^{*,l}$$

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 on page 3-105 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:

$H_m^l - H_m^{ig}$ = $\sum_A x_A \left( H_A^{*,l} - H_A^{*,ig} \right) + H_m^{E,l}$

$H_m^{E,l}$ = $-RT^2 \sum_B x_B \left( \frac{\delta \ln \gamma_B}{\delta T} \right)$

$H_A^{*,l} - H_A^{*,ig}$ = 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:

$H_i^{ref,l}$ = Reference enthalpy for liquid state at $T_i^{ref,l}$

= 0 at $T_i^{ref,l}$ of 273.15 K by default

$C_{p,i}^{*,l}$ = 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:

$$H_i^{*,v} = H_i^{*,ig} + \Delta H_{v,i}^*\left(T, P\right)$$

Where:

$\Delta H_{v,i}^*\left(T, P\right)$ = 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:

$$\overline{V}^o = a_1 + a_2\left(\frac{1}{p+\psi}\right) + \left[a_3 + a_4\left(\frac{1}{p+\psi}\right)\right]\left(\frac{1}{T-\theta}\right) - \omega \quad Q + \left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial p}\right)_T$$

$$\overline{C}_p^o = c_1 + \frac{c_2}{(T-\theta)^2} - \frac{2T}{(T-\theta)^3}\left[a_3(p-p_r) + a_4\ln\left(\frac{p+\psi}{p_r+\psi}\right)\right] + \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_p$$
$$- T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_p$$

$$\overline{S}^o = \overline{S}_{Tr\,Pr}^o + c_1\ln\left(\frac{T}{T_r}\right) - \frac{c_2}{\theta}\left[\frac{1}{T-\theta} - \frac{1}{T_r-\theta} + \frac{1}{\theta}\ln\left(\frac{T_r(T-\theta)}{T(T_r-\theta)}\right)\right]$$
$$+ \left(\frac{1}{T-\theta}\right)^2\left[a_3(p-p_r) + a_4\ln\left(\frac{p+\psi}{p_r+\psi}\right)\right] + \omega Y - \left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_p - \omega_{Tr\,Pr}Y_{Tr\,Pr}$$

$$\Delta\overline{H}^o = \Delta\overline{H}_f^o + c_1(T-T_r) - c_2\left(\frac{1}{T-\theta} - \frac{1}{T_r-\theta}\right) + a_1(p-p_r) + a_2\ln\left(\frac{p+\psi}{p_r+\psi}\right)$$
$$+ \left(\frac{2T-\theta}{(T-\theta)^2}\right)\left[a_3(p-p_r) + a_4\ln\left(\frac{p+\psi}{p_r+\psi}\right)\right] + \omega\left(\frac{1}{\varepsilon}-1\right) + \omega TY$$
$$- T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_p - \omega_{Tr\,Pr}\left(\frac{1}{\varepsilon_{Tr\,Pr}}-1\right) - \omega_{Tr\,Pr}T_r Y_{Tr\,Pr}$$

$$\Delta\overline{G}^o = \Delta\overline{G}_f^o - \overline{S}_{Tr\,Pr}^o(T-T_r) - c_1\left[T\ln\left(\frac{T}{T_r}\right) - T + T_r\right] + a_1(p-p_r) + a_2\ln\left(\frac{p+\psi}{p_r+\psi}\right)$$
$$- c_2\left[\left(\frac{1}{T-\theta} - \frac{1}{T_r-\theta}\right)\left(\frac{\theta-T}{\theta}\right) - \frac{T}{\theta^2}\ln\left(\frac{T_r(T-\theta)}{T(T_r-\theta)}\right)\right]$$
$$+ \frac{1}{T-\theta}\left[a_3(p-p_r) + a_4\ln\left(\frac{p+\psi}{p_r+\psi}\right)\right] + \omega\left(\frac{1}{\varepsilon}-1\right)$$
$$- \omega_{Tr\,Pr}\left(\frac{1}{\varepsilon_{Tr\,Pr}}-1\right) + \omega_{Tr\,Pr}Y_{Tr\,Pr}(T-T_r)$$

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:

| | | |
|---|---|---|
| $\psi$ | = | Pressure constant for a solvent (2600 bar for water) |
| $\theta$ | = | Temperature constant for a solvent (228 K for water) |
| $\omega$ | = | Born coefficient |
| $\varepsilon$ | = | 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 [†] | $a_1, \dots, a_4$ | 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 Aspen Plus. The following table  provides an overview of the available models. This table lists the Aspen Plus 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 MUL0H2O | V L | X 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** | | | | |
| Chung-Lee-StarlingThermal Conductivtity | KV0CLS2, KV2CLS2, KL0CLS2, KL2CLS2 | V L | X | X |
| IAPS Thermal Conductivity | KV0H2O KL0H2O | V L | X 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 | — |

*Continued*

**Thermal conductivity models (continued)**

| Viscosity models | Model name | Phase(s) | Pure | Mixture |
|---|---|---|---|---|
| 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** | | | | |
| 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** | | | | |
| API Surface Tension | SIG2API | L | — | X |
| Hakim-Steinberg-Stiel/DIPPR /IK-CAPE | SIG0HSS, SIG2HSS | L | X | — |
| IAPS thermal conductivity | SIG0H2O | L | X | — |
| Onsager-Samaras Electrolyte Correction | SIG2ONSG | L | — | X |

# Viscosity Models

Aspen Plus 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 |

*Continued*

| Model | Type |
|---|---|
| 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 $k_{ij}$ and $m_{ij}$ 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:

$$\ln \eta_i^{*,l} = A_i + \frac{B_i}{T} + C_i \ln T \ \text{ for } \ T_l \leq T \leq T_h$$

| 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:

$$\ln \eta_i^{*,l} = C_{1i} + C_{2i}/T + C_{3i} \ln T + C_{4i}T^{C_{5i}} \ \text{ for } \ C_{6i} \leq T \leq C_{7i}$$

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.*

## 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.

## 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, Aspen Plus 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, Aspen Plus 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 |

## 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:

$$\eta_i^{*,v}(p=0) = 2.669 \times 10^{-26} \frac{\sqrt{M_i T}}{\sigma_i^2 \Omega_\eta}$$

Where:

$$\Omega_\eta = fcn(T, \varepsilon_i/k)$$

Polar parameter $\delta$ is used to determine whether to use the Stockmayer or Lennard-Jones potential parameters: $\varepsilon/k$ (energy parameter) and $\sigma$ (collision diameter). To calculate $\delta$, 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 | $\sigma_i^{ST}$ | $fcn(T_{bi}, V_{bi}, p_i)$ | X | — | — | LENGTH |
| LJPAR/1 | $(\varepsilon_i/k)^{LJ}$ | $fcn(T_{ci}, \omega_i)$ | X | — | — | TEMPERATURE |
| LJPAR/2 | $\sigma_i^{LJ}$ | $fcn(T_{ci}, p_{ci}, \omega_i)$ | 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.*

### 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.

### IK-CAPE Vapor Viscosity

The IK-CAPE vapor viscosity model includes both the Sutherland equation and the polynomial equation.

### Sutherland Equation

$$\eta_i^{*,v}\left(p=0\right)= C_{1i}T^{0.5}\Big/\left(1+ C_{2i}/T\right)\text{for}\, C_{3i} \leq T \leq C_{4i}$$

If the parameter MUVSUT is available, Aspen Plus 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, Aspen Plus 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 |

# 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 $\Phi_{ij}$, the formulation by Brokaw is used:

$$\Phi_{ij} = \left[ \frac{\eta_i^{*,v}(p=0)}{\eta_j^{*,v}} \right]$$

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 $\delta$ is used to determine whether to use the Stockmayer or Lennard-Jones potential parameters: $\varepsilon/k$ (energy parameter ) and $\sigma$ (collision diameter). To calculate $\delta$, 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 | $\left(\varepsilon_i / k\right)^{ST}$ | $fcn(T_{bi}, V_{bi}, p_i)$ | — | X | — | TEMPERATURE |
| STKPAR/2 | $\sigma_i^{ST}$ | $fcn(T_{bi}, V_{bi}, p_i)$ | 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 $\kappa'$ 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:

$$V_{cij} \quad = \quad \left(1 - \xi_{ij}\right)\left(V_{ci} V_{cj}\right)^{1/2}$$

$$\xi_{ij} \quad = \quad \text{0 (in almost all cases)}$$

$$T_{cij} \quad = \quad \left(1 - \zeta_{ij}\right)\left(T_{ci} T_{cj}\right)^{1/2}$$

$$\zeta_{ij} \quad = \quad \text{0 (in almost all cases)}$$

$$\omega_{ij} \quad = \quad \frac{\left(\omega_i + \omega_j\right)}{2}$$

$$M_{ij} \quad = \quad \left[ \frac{2 M_i M_j}{\left(M_i + M_j\right)} \right]^{1/2}$$

$$\kappa_{ij} \quad = \quad \left(\kappa_i \kappa_j\right)^{1/2}$$

| 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 | $5 \times 10^{-24}$ | DIPOLEMOMENT |
| OMGCLS[†] | $\omega_i$ | OMEGA | x | -0.5 | 2.0 | — |
| CLSK[†] | $\kappa_i$ | 0.0 | x | 0.0 | 0.5 | — |
| CLSKV[†] | $\xi_{ij}$ | 0.0 | x | -0.5 | -0.5 | — |
| CLSKT[†] | $\zeta_{ij}$ | 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:

$$\eta^v = \frac{40.785(MT)^{1/2} F_C}{V_{cm}^{2/3} \Omega_\eta} f_1 + \frac{36.344(MT_c)^{1/2}}{V_{cm}^{2/3}} f_2$$

With:

$$f_1 \quad = \quad fcn(\rho_m, V_{cm}, \omega, p_r, \kappa)$$

$$f_2 \quad = \quad fcn(\omega, p_r, \kappa)$$

$$F_2 \quad = \quad fcn(\omega, p_r, \kappa)$$

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 $\kappa$ 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:**

$$V_{cij} = \left(1 - \xi_{ij}\right)\left(V_{ci}V_{cj}\right)^{1/2}$$

$$\xi_{ij} = \textbf{0 (in almost all cases)}$$

$$T_{cij} = \left(1 - \zeta_{ij}\right)\left(T_{ci}T_{cj}\right)^{1/2}$$

$$\zeta_{ij} = \textbf{0 (in almost all cases)}$$

$$\omega_{ij} = \frac{\left(\omega_i + \omega_j\right)}{2}$$

$$M_{ij} = \left[\frac{2M_i M_j}{\left(M_i + M_j\right)}\right]^{1/2}$$

$$\kappa_{ij} = \left(\kappa_i \kappa_j\right)^{1/2}$$

| 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 | $5 \times 10^{-24}$ | DIPOLEMOMENT |
| OMGCLS[†] | $\omega_i$ | OMEGA | x | -0.5 | 2.0 | — |
| CLSK[†] | $\kappa_i$ | 0.0 | x | 0.0 | 0.5 | — |
| CLSKV[†] | $\xi_{ij}$ | 0.0 | x | -0.5 | -0.5 | — |
| CLSKT[†] | $\zeta_{ij}$ | 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 $\xi$ is:

$$\xi \quad = \quad N_A^2 \frac{T_c^{1/6}}{M^{1/2} p_c^{2/3}}$$

$$T_c \quad = \quad \sum_i y_i T_{ci}$$

$$M \quad = \quad \sum_i y_i M_i$$

$$p_c \quad = \quad \frac{Z_{cm} R T_c}{V_{cm}}$$

$$V_{cm} \quad = \quad \sum_i y_i V_{ci}$$

$$Z_{cm} \quad = \quad \sum_i y_i Z_{ci}$$

$$\rho_{rm} \quad = \quad \frac{V_{cm}}{V_m^v}$$

The parameter <$EV sub m sup {^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:

$$\eta^l = \eta_{solv}\left(1 + \sum_{ca} \Delta\eta_{ca}^l\right) \qquad (1)$$

Where:

$\eta_{solv}$ = 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:

$$\Delta\eta_{ca}^l = A_{ca}\sqrt{c_{ca}^a} + B_{ca}c_{ca}^a \quad 2)$$

Where:

$c_{ca}^a = \dfrac{x_{ca}^a}{V_m^l}$    =    Concentration of apparent electrolyte ca      (3)

$x_{ca}^a$    =    Mole fraction of apparent electrolyte *ca*

$A_{ca}$    =

$$\dfrac{1.45}{\eta_{solv}^l(2\varepsilon T)^{\frac{1}{2}}}\left[\dfrac{L_c + L_a}{4L_cL_a} - \dfrac{L_c - L_a}{\left(3 + \sqrt{2}\,L_cL_a(L_c + L_a)\right)}\right] \quad (4)$$

$L_a$    =    $l_{a,1} + l_{a,2}T$      (5)

$L_c$    =    $l_{c,1} + l_{c,2}T$      (6)

$B_{ca}$    =    $\left(b_{c,1} + b_{c,2}T\right) + \left(b_{a,1} + b_{a,2}T\right)$      (7)

## Breslau-Miller

The Breslau-Miller equation is:

$$\Delta\eta_{ca}^l = 2.5V_e c_{ca}^a + 10.05V_e\left(c_{ca}^a\right)^2 \quad (8)$$

Where the effective volume $V_c$ is given by:

$$V_e = \dfrac{(B_{ca} - 0.002)}{2.60} \quad \text{for salts involving univalent ions} \quad (9)$$

$$V_e = \dfrac{(B_{ca} - 0.011)}{5.06} \quad \text{for other salts} \quad (9a)$$

## Carbonell

The Carbonell equation is:

$$\Delta\eta_{ca}^l = \exp\left[0.48193\left(\sum_k M_k x_k^a\right)\dfrac{c_{ca}^a}{T}\right] - 1.0 \quad (10)$$

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:

$$\eta^l \varepsilon = \left( \eta^l \varepsilon \right)^0 + \omega \left( \eta^l \varepsilon \right)^1$$

Where:

$$\left( \eta^l \varepsilon \right)^0 = fcn(T, x_i, T_{ci})$$

$$\left( \eta^l \varepsilon \right)^1 = fcn(T, x_i, T_{ci})$$

$$\varepsilon = fcn(x_i, M_i, T_{ci}, p_{ci}, \omega_i)$$

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

| 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 | $\omega_i$ | — | — | -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:

$$\xi = N_A^2\,\frac{T_c^{\frac{1}{6}}}{M^{\frac{1}{2}}p_c^{\frac{2}{3}}}$$

The pressure correction factor $Y$ is:

$$Y = fcn(p_r, T_r)$$

The polar and quantum correction factors at high and low pressure are:

$$F_P \quad = \quad fcn\big(Y, F_P(p=0)\big)$$

$$F_Q \quad = \quad fcn\big(Y, F_Q(p=0)\big)$$

$$F_{Pi}(p=0) \quad = \quad fcn(T_{ri}, p_{ci}, Z_{ci}, \boldsymbol{p}_i)$$

$$F_{Qi}(p=0) \quad = \quad fcn(T_{ri}), \text{ but is only nonunity for the quantum gates } i = H_2, E_2 \text{ and } He.$$

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 | $p_i$ | — | — | 0.0 | $5 \times 10^{-24}$ | 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:

$$\eta = fcn(t, p, \bar{x}, M_i, T_{ci}, p_{ci}, V_{ci}, Z_{ci}, \omega_i)$$

Where:

The parameter $\bar{x}$ 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 | $\omega_i$ | 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

Aspen Plus 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 |

| Model | Type |
|-------|------|
| 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:

$$f_1 \quad = \quad fcn(\rho_m, \omega, \boldsymbol{p}_r, \kappa)$$

$$f_2 \quad = \quad fcn(T_c, M, V_{cm}, \rho_{rm}, \omega, \boldsymbol{p}_r, \kappa)$$

$$\Psi \quad = \quad fcn(C_v, \omega, T_r)$$

$\eta(p=0)$ 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 $\boldsymbol{p}_r$ is the reduced dipolemoment:

$$\boldsymbol{p}_r = 4.152 \frac{\boldsymbol{p}}{\left(V_{cm} T_c^{1/2}\right)}$$

The polar parameter $\kappa$ 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 on page 3-136.)

$$C_v = \sum_i x_i C_{v,i}$$

$$M = \left[ \frac{\sum_i \sum_j x_i x_j T_{cij} V_{cij}^{\frac{2}{3}} M_{ij}}{T_c V_{cm}^{\frac{2}{3}}} \right]^2$$

$$\omega = \frac{\sum_i \sum_j x_i x_j \omega_{ij} V_{cij}}{V_{cm}}$$

$$p_r = \frac{131.3p}{V_{cm} T_c^{\frac{1}{2}}}$$

$$p^4 = \frac{\sum_i \sum_j x_i x_j p_i^2 p_j^2 V_c}{V_{cij}}$$

$$\kappa = \sum_i \sum_j x_i x_j \kappa_{ij}$$

Where:

$$V_{cij} \quad = \quad \left(1 - \xi_{ij}\right)\left(V_{ci} V_{cj}\right)\frac{1}{2}$$

$$\xi_{ij} \quad = \quad \textbf{0 (in almost all cases)}$$

$$T_{cij} \quad = \quad \left(1 - \zeta_{ij}\right)\left(T_{ci} T_{cj}\right)^{\frac{1}{2}}$$

$$\zeta_{ij} \quad = \quad \textbf{0 (in almost all cases)}$$

$$\omega_{ij} \quad = \quad \frac{\left(\omega_i + \omega_j\right)}{2}$$

$$M_{ij} \quad = \quad \left[\frac{2 M_i M_j}{\left(M_i + M_j\right)}\right]^{\frac{1}{2}}$$

$$\kappa_{ij} \quad = \quad \left(\kappa_i \kappa_j\right)^{\frac{1}{2}}$$

| 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 | — |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| MUP | $p_i$ | — | — | 0.0 | $5 \times 10^{-24}$ | DIPOLEMOMENT |
| OMGCLS[†] | $\omega_i$ | OMEGA | x | -0.5 | 2.0 | — |
| CLSK[†] | $\kappa_i$ | 0.0 | x | 0.0 | 0.5 | — |
| CLSKV[†] | $\xi_{ij}$ | 0.0 | x | -0.5 | -0.5 | — |
| CLSKT[†] | $\zeta_{ij}$ | 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.

## 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:

| | | |
|---|---|---|
| $\lambda_{solv}^l$ | = | 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):

$$\lambda_i^{*,l} = \frac{1.1053152}{M_i^{1/2}}\left(\frac{3 + 20(1 - T_{ri})^{2/3}}{3 + 20(1 - T_{bri})^{2/3}}\right)$$

Where:

$$T_{bri} \quad = \quad T_{bi}/T_{ci}$$

$$T_{ri} \quad = \quad T/T_{ci}$$

| 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 | $C_{2i}, \ldots, C_{5i}$ | 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, Aspen Plus 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 | $C_{2i}, \ldots, C_{10i}$ | 0 | x | — | — | THERMAL-CONDUCTIVITY, TEMPERATURE |
| KLPO/11 | $C_{11i}$ | 0 | x | — | — | TEMPERATURE |
| KLPO/12 | $C_{12i}$ | 1000 | x | — | — | TEMPERATURE |

## 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 calcualted by two equations:

- Sato-Riedel
- DIPPR
- IK-CAPE

See the Sato-Riedel/DIPPR/IK-CAPE model for descriptions.

### 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.

## 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:

$\eta_i^{*,v} \left( p = 0 \right)$ 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 |

[†]    *If elements 2, 3, or 4 are non-zero, absolute temperature units are assumed for elements 1 through 4.*

## 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.

### 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, Aspen Plus 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 |

## 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:

$$\rho_{rm} \quad = \quad \sum_i y_i \frac{V_{ci}}{V_m^v}$$

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:

$$\lambda = fcn\left(T, P, \overline{x}, M_i, T_{ci}, p_{ci}, V_{ci}, Z_{ci}, \omega_i, C_{p_i}^{*,ig}\right)$$

Where:

| | | |
|---|---|---|
| $\overline{x}$ | = | Mole fraction vector |
| $C_{p_i}^{*,ig}$ | = | Ideal gas heat capacity calculated using the Aspen Plus 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 | $\omega_i$ | 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

Aspen Plus 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:

$$\Omega_D \quad = \quad fcn(T, \varepsilon_{ij}/k)$$

The binary size and energy parameters are defined as:

$$\sigma_{ij} \quad = \quad \frac{(\sigma_i + \sigma_j)}{2}$$

$$\varepsilon_{ij} \quad = \quad (\varepsilon_i \varepsilon_j)^{\frac{1}{2}}$$

Polar parameter $\delta$ is used to determine whether to use the Stockmayer or Lennard-Jones potential parameters: $\varepsilon/k$ (energy parameter ) and $\sigma$ (collision diameter). To calculate $\delta$, the dipole moment $\boldsymbol{p}$, 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 | $\boldsymbol{p}_i$ | — | — | 0.0 | $5 \times 10^{-24}$ | DIPOLEMOMENT |
| STKPAR/1 | $(\varepsilon/k)_{ST}$ | $fcn(\boldsymbol{p}_i, T_{bi}, V_{bi})^x$ | — | — | | TEMPERATURE |
| STKPAR/2 | $\sigma_{ST}$ | $fcn(\boldsymbol{p}_i, T_{bi}, V_{bi})^x$ | — | — | | LENGTH |
| LJPAR/1 | $(\varepsilon/k)_{LJ}$ | $fcn(T_{ci}, \omega_i)$ | x | — | | TEMPERATURE |
| LJPAR/2 | $\sigma_{LJ}$ | $fcn(T_{ci}, \boldsymbol{p}_i, \omega_i)^x$ | — | — | | 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) on page 3-159.)

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 $\rho_m^v$ 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) on page 3-161.)

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:

$$D_i = \left( \frac{RT}{z_i F^2} \right) (l_{1,i} + l_{e,i} T) \sum_k x_k \qquad (1)$$

Where:

| | | |
|---|---|---|
| F | = | $9.65 \times 10^7$ 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:

$$D_{ij} = \frac{\left(D_i + D_j\right)}{2}$$

| 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:

$$D_{ij}^{\infty,l} = 1.17282 \times 10^{-16} \frac{\left(\varphi_j M_j\right)^{\frac{1}{2}} T}{n_j^l \left(V_{bi}^{*,l}\right)^{0.6}}$$

Where $i$ is the diffusing solute and $j$ the solvent:

| | | |
|---|---|---|
| $\varphi_j$ | = | Association factor of solvent |
| $n_j^l$ | = | Liquid viscosity of the solvent simulation. 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:

$$D_i^l = 1.17282 \times 10^{-16} \frac{(\varphi M)^{1/2} T}{n^l \left( V_{bi}^{*,l} \right)^{0.6}}$$

With:

$$\varphi M = \frac{\sum_{j \neq i} x_j \varphi_j M_j}{\sum_{j \neq i} x_j}$$

Where:

$\varphi_j$  =  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

Aspen Plus 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 $\chi_i$ 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 |

| Parameter Name/Element | Symbol | Default | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|
| OMEGA | $\omega_i$ | — | -0.5 | 2.0 | — |
| CHI | $\chi_i$ | 0 | — | — | — |

## DIPPR Liquid Surface Tension

The DIPPR equation for liquid surface tension is:

$$\sigma_i^{*,l} = C_{1i}\left(1 - T_{ri}\right)^{\left(C_{2i} + C_{3i}T_{ri} + C_{4i}T_{ri}^2 + C_{5i}T_{ri}^3\right)} \quad \text{for} \quad C_{6i} \le T \le C_{7i}$$

Where:

$$T_{ri} \quad = \quad T/T_{ci}$$

If the SIGDIP parameters for a given component are available, Aspen Plus 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 |

## 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.

## IK-CAPE Polynomial

The IK-CAPE model is a polynomial equation containing 10 terms. If the parameter SIGPO is available, Aspen Plus 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 |

# Onsager-Samaras

The Onsager-Samaras model calculates the correction to the liquid mixture surface tension of a solvent mixture, due to the presence of electrolytes:

$$\sigma = \sigma_{solv} + \sum_{ca} x_{ca}^a \Delta\sigma_{ca} \tag{1}$$

Where:

$\sigma_{solv}$ = 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:

$$\Delta\sigma_{ca} = \frac{80.0}{\varepsilon_{solv}} c_{ca}^a \log\left\{\frac{1.13\text{x}10^{-13}(\varepsilon_{solv}T)^3}{c_{ca}^a}\right\} \tag{2}$$

Where:

$\varepsilon_{solv}$ = 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 Aspen Plus. 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 for process simulation, 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**

| | | |
|---|---|---|
| General coal enthalpy model | HCOALGEN | S |
| IGT coal density model | DCOALIGT | S |
| IGT char density model | DCHARIGT | S |

# General Enthalpy and Density Models

Aspen Plus 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:

$$\rho_i^s = \frac{1}{\sum_i \frac{w_{ij}}{\rho_{ij}}}$$

$$\rho_{i,j}^s = a_{i,j1} + a_{i,j2}T + a_{i,j3}T^2 + a_{i,j4}T^3$$

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 | Units |
|---|---|---|---|---|---|---|
| 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 | — | — | — | † |
| HCGEN/2+4 | $a_{i,j2}$ | x | 0 | — | — | † |
| HCGEN/3+4 (J-1) | $a_{i,j3}$ | x | 0 | — | — | † |
| HCGEN/4+4 (J-1) | $a_{i,j4}$ | x | 0 | — | — | † |

† *The units 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 Aspen Plus 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 Aspen Plus 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 |
| $w^d$ | = | The value on a dry basis |
| $w_{H_2O}$ | = | 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:

| | | |
|---|---|---|
| $\Delta w^d$ | = | 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 |
| $\rho$ | = | 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 Aspen Plus 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 lists model option codes for HCLOALGEN. The table is followed by a detailed description of the calculations used for each correlation.

The correlations are described inthe 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 , ... , $ncn$ |
| 1 | = | Moisture |
| 2 | = | Fixed carbon |
| 3 | = | Primary volatile matter |
| 4 | = | Secondary volatile matter |
| 5 | = | Ash |
| $w_j$ | = | Mass fraction of $j$th 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 | $a_{i,22}$ | $6.8 \times 10^{-4}$ |
| CP1C/7 | $a_{i,23}$ | $-4.2 \times 10^{-7}$ |
| CP1C/8 | $a_{i,24}$ | 0 |
| CP1C/9 | $a_{i,31}$ | 0.395 |
| CP1C/10 | $a_{i,32}$ | $8.1 \times 10^{-4}$ |
| CP1C/11 | $a_{i,33}$ | 0 |
| CP1C/12 | $a_{i,34}$ | 0 |

*Continued*

| Parameter Name/Element | Symbol | Default |
|---|---|---|
| CP1C/13 | $a_{i,41}$ | 0.71 |
| CP1C/14 | $a_{i,42}$ | $6.1 \times 10^{-4}$ |
| CP1C/15 | $a_{i,43}$ | 0 |
| CP1C/16 | $a_{i,44}$ | 0 |
| CP1C/17 | $a_{i,51}$ | 0.18 |
| CP1C/18 | $a_{i,52}$ | $1.4 \times 10^{-4}$ |
| 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 | $a_{2i}$ | $-7.576 \times 10^{-3}$ |
| CP2C/3 | $a_{3i}$ | $8.793 \times 10^{-5}$ |
| CP2C/4 | $a_{4i}$ | $-2.587 \times 10^{-7}$ |

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 ULFANAL ROXANAL |
| | 5 | IGT correlation | CIGTC | ULTANAL ROXANAL |
| | 6 | User input value | HCOMB | ULTANAL ROXANAL |
| **2 Standard Heat of Formation** | | | | |
| | 1 | Heat-of-combusion-based correlation | — | ULTANAL ULFANAL |
| | 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 | — | — |

# 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 $\rho_i^{dm}$ is good for a wide range of hydrogen contents, including anthracities and high temperature cokes. The standard deviation of this correlation for a set of 190 points collected by IGT from the literature was

$12 \times 10^{-6} \ \mathrm{m^3/kg}$. 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 $2.2 \times 10^3$ to $2.26 \times 10^3 \ \mathrm{kg/m^3}$. Densities of nongraphitic high-temperature carbons (derived from chars) range from $2.0 \times 10^3$ to $2.2 \times 10^3 \ \mathrm{kg/m^3}$. 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.

IGT (Institute of Gas Technology), *Coal Conversion Systems Technical Data Book*, Section PMa. 44.1, 1976.

N.Y. Kirov, "Specific Heats and Total Heat Contents of Coals and Related Materials are Elevated Temperatures," *BCURA Monthly Bulletin*, (1965), pp. 29, 33.

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.

# 4      Property Calculation Methods and Routes

In Aspen Plus 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 simulation. 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 Aspen Plus, provides guidelines for choosing an appropriate property method for your simulation, and describes how to modify property methods to suit your simulation needs by replacing property models.

This chapter discusses:
- Major, subordinate, and intermediate properties in Aspen Plus
- 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:

$$\varphi_i^{*,l} \quad = \quad \varphi_i^{*,v} \frac{p_i^{*,l}}{p} \tag{2}$$

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 $\left(\gamma_i, \varphi_i^{*,l}, p_i^{*,l}\right)$ and state variables $\left(x_i, p\right)$. 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 $\left(\gamma_i\right)$
- 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 $\gamma_i$ 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 Plus 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 Aspen Plus. 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 Aspen Plus 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 Aspen Plus. 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 Aspen Plus

The following properties may be required by unit operations in Aspen Plus simulations:

• 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 Aspen Plus are called *major properties* and are listed in the table labeled Major Properties in Aspen Plus on page 4-4. 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 Aspen Plus on page 4-6 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 Aspen Plus on page 4-8 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 Aspen Plus*

| 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 | $\varphi_i^{v}$ | Vapor fugacity coefficient of a component in a mixture |
| PHILMX | $\varphi_i^{l}$ | Liquid fugacity coefficient of a component in a mixture |
| PHISMX | $\varphi_i^{s}$ | 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 |
| 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 |

*Continued*

| Property Name | Symbol | Description |
|---|---|---|
| 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<F20MI> |
| MUV | $\eta_i^{*,v}$ | Vapor pure component viscosity |
| MUL | $\eta_i^{*,l}$ | Liquid pure component viscosity |
| MUVMX | $\eta_i^v$ | Vapor mixture viscosity |
| MULMX | $\eta_i^l$ | 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 | $\lambda_i^v$ | Vapor mixture thermal conductivity |
| KLMX | $\lambda_i^l$ | Liquid mixture thermal conductivity |
| KSMX | $\lambda_i^s$ | 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 | $\sigma^l$ | Mixture surface tension |

## *Subordinate Properties in Aspen Plus*

| 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 |
| 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 |

*Continued*

| Property Name | Symbol | Description |
|---|---|---|
| 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 | $\theta^E$ | Liquid activity coefficient pressure correction, symmetric convention |
| GAMPC1 | $\theta^{*E}$ | Liquid activity coefficient pressure correction, asymmetric convention |
| HNRYPC | $\theta_{iA}^\infty$ | 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 | $\lambda_i^{*,v}(p=0) - \lambda_i^{*,v}(p=0)$ | Pure component vapor thermal conductivity pressure correction |
| KVMXLP | $\lambda^v(p=0)$ | Low pressure, vapor mixture thermal conductivity |
| KVMXPC | $\lambda^v(p) - \lambda^v(p=0)$ | Vapor mixture thermal conductivity pressure correction |

## *Intermediate Properties in Aspen Plus*

| Property Name | Symbol | Description |
|---|---|---|
| GAMMA | $\gamma$ | Liquid phase activity coefficient |
| GAMUS | $\gamma^*$ | Liquid phase activity coefficient, unsymmetric convention |
| GAMMAS | $\gamma^s$ | 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 Aspen Plus.

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 Aspen Plus might not be
exhaustive, but multiple methods for one property also exist.

All physical property methods available for calculating major and subordinate
properties in Aspen Plus 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 1   Methods for calculating liquid mixture enthalpy**

From the table labeled Liquid Enthalpy Methods on page 4-18, 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 two methods as listed in the table labeled Liquid Enthalpy Methods on page 4-18. 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 |
|---|---|---|---|---|
| $\varphi_i^{*,v}$<br>PHIV | Major | 1 | Specified model | $\varphi_i^{*,v}$ Model name |
| $\varphi_i^v$<br>PHIVMX | Major | 1 | Specified model | $\varphi_i^v$ Model name (Default: $\varphi_i^v = 1$) |
| | | 2 | $\varphi_i^v = f\left( y_i, \varphi_i^{*,v} \right)$ | $\varphi_i^{*,v}$ Route ID<br>$\varphi_i^v$ Model name |
| | | 3 | $\varphi_i^v = f\left( \gamma_i \right)$ | $\gamma_i$ Model name<br>$\varphi_i^v$ 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 | $$\frac{\varphi_i^{*,v}\left(T, p_i^{*,l}\right) p_i^{*,l} \theta_i^{*,l}}{p}$$ | $p^{*,l}$ 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 |
| $\varphi_i^{l}$ PHILMX | Major | 1 | Specified model | $\varphi_i^{l}$ Model name |
| | | 2 | $\gamma_i \varphi_i^{*,l} \theta_i^{E}$ | $\gamma_i$ Model name (Default: $\gamma_i = 1$) $\varphi_i^{*,l}$ Route ID $\theta_i^{E}$ Route ID (Default: $\theta_i^{E} = 1$) |
| | | 3 | Unsymmetric Convention For subcritical components (A or B): | $\varphi_A^{*,l}$ Route ID |

*Continued*

## *Liquid Fugacity Coefficient Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | | $\varphi_A^l = \delta_A \gamma_A \varphi_A^{*,l}$ | $\gamma_A$ 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: $$\ln \delta_A = \frac{w_A}{x_A} \sum_j x_j \left[ \ln \left( \frac{H_{iA}}{\gamma_{jA}^\infty} \right) - \ln \left( \frac{H_j}{\gamma_j^\infty} \right) \right]$$ | $H_{jA}$ 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 |
| | | | $$\ln \gamma_i^\infty = \lim_{\Sigma_j x_j \to 0} (\ln \gamma_i)$$ | $w_B$ 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 ) |
| | | 4 | $\gamma_i \varphi_i^{*,l} \theta_i^E$ | $\gamma_i$ Model name (Default: $\gamma_i = 1$) $\varphi_i^{*,l}$ Route ID $\theta_i^E$ 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 |

*Continued*

## *Liquid Fugacity Coefficient Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | | $$\varphi_A^l = \delta_A \gamma_A \varphi_A^{*,l}$$ | $\gamma_A$ Model name (Default: $\gamma_A = 1$) |
| | | | Where: $$\gamma_A = f\left(x^t\right)$$ | $x^t$ Route ID |
| | | | For supercritical components (i or j) $$\varphi_i^l = \gamma_i \left(\frac{H_i}{p\gamma_i^\infty}\right)$$ | |
| | | | Where: $$\ln \delta_A = \frac{W_A}{X_A} \sum_j x_j \left[ \ln\left(\frac{H_{iA}}{\gamma_{jA}^\infty}\right) - \ln\left(\frac{H_j}{\gamma_j^\infty}\right) \right]$$ | $H_{jA}$ 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 |
| | | | $$\ln \gamma_i^\infty = \lim_{\sum_j x_j \to 0} \left(\ln \gamma_i\right)$$ | $w_B$ Model option code (see Model Option Code Help) |
| | | | $$\sum_B w_B = 1$$ | Method Option code |
| | | | | 0: Do not calculate $H_i$<br>1: Calculate $H_i$<br>(Default = 0 ) |
| | | 6 | $$\varphi_i^l = f(\gamma_i)$$ | $\gamma_i$ Model name<br>$\varphi_i^l$ Model name |
| $x^t$<br>XTRUE | Subord. | 1 | $$x^t = f(T, x_i, \gamma_i, \text{Chemistry})$$ | $\gamma_i$ Model name |
| $\theta_i^E$<br>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 |

*Continued*

## *Liquid Fugacity Coefficient Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | | | Integration option code |
| | | | | (Default: 1 point) |
| | | 2 | Specified model | $\theta_i^E$ Model name |
| $\theta_i^{*,E}$ GAMPC1 | Subord. | 1 | $\exp\left( \dfrac{1}{RT} \displaystyle\int_{p^{ref}}^{p} V_i^l \, dp \right)$ | $V_i^l$ 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 |
| | | | | $\theta_{iA}^{\infty}$ Route ID |
| | | | | (Default: $\theta_{iA}^{\infty} = 1$) |
| | | | | $p^{ref}$ defined by the $p^{ref}$ option code of HNRYPC |
| $\theta_{iA}^{\infty}$ HNRYPC | Subord. | 1 | $\exp\left( \dfrac{1}{RT} \displaystyle\int_{p^{ref}}^{p} V_i^l \, dp \right)$ | $p_A^{*,l}$ 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) |
| | | | | $V_i^{\infty}$ Model name |

*Continued*

## *Liquid Fugacity Coefficient Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | | | Integration code |
| | | | | (Default: 1 point) |
| | | 2 | Specified model | $\theta_{iA}^{\infty}$ 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 <br> $\varphi_i^{*,v}$ Model name <br> (Default: $\varphi_i^{*,v}$ = 1) <br> $\theta_i^{*,s}$ Route ID <br> (Default: $\theta_i^{*,s}$ = 1) |
| | | 3 | $\varphi_i^{*,s}\, \varphi_i^{*,l}$ | $\varphi_i^{*,s}$ Model name <br> $\varphi_i^{*,l}$ 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 <br> $V_i^{*,s}$ Model name <br> Integration option code <br> (Default: 1 point) |
| | | 2 | Specified model | $\theta_i^{*,s}$ Model name |
| $\varphi_i^{s}$ PHISMX | Major | 1 | Specified model | $\varphi_i^{s}$ Model name |
| | | 2 | $\varphi_i^{s} = f\left(x_i^{s}, \varphi_i^{*,s}\right)$ | $\varphi_i^{*,s}$ Route ID <br> $\varphi_i^{s}$ Model name |
| | | 3 | $\gamma_i^{s} \varphi_i^{*,s}$ | $\gamma_i^{s}$ Model name <br> $\varphi_i^{*,s}$ Route ID |

## *Vapor Enthalpy Methods*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $H_i^{*,v}$ <br> 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 <br> (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) |
| | | 3 | $H_i^{*,l} + \Delta_{vap} H_i^*$ | $H_i^{*,l}$ Route ID <br> $\Delta_{vap} H_i^*$ Model name |
| $H_i^{*,v} - H_i^{*,ig}$ <br> 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 |
| $H_m^v$ <br> 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 <br> (Default: $H_m^v - H_m^{ig} = 0$) |
| $H_m^v - H_m^{ig}$ <br> DHVMX | Subord. | 1 | Specified model | $\left( H_m^v - H_m^{ig} \right)$ Model name |
| | | 2 | $-RT^2 \displaystyle\sum_i y_i \left( \dfrac{\partial \ln \varphi_i^v}{\partial T} \right)$ | $\varphi_i^v$ Model name |

### *Liquid Enthalpy Methods*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $H_i^{*,l}$ <br> 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 |
| $H_i^{*,l} - H_i^{*,ig}$ <br><br> 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 | $\left( H_i^{*,v}\left(T, p_i^{*,l}\right) - H_i^{*,ig}\left(T\right) \right) - \Delta_{vap} H_i^{*}\left(T\right)$ $+ \left( H_i^{*,l}\left(T,p\right) - H_i^{*,l}\left(T, p_i^{*,l}\right) \right)$ | $p_i^{l}$ Model name <br> $\left( H_i^{*,v} - H_i^{*,ig} \right)$ <br> Route ID <br> (Default: $H_i^{*,v} - H_i^{*,ig}$ $= 0$ ) <br> $\Delta_{vap} H_i^{l}$ Model name <br> $\left( H_i^{*,l}\left(T,p\right) - H_i^{*,l}\left(T, p_i^{*,l}\right) \right)$ <br> Route ID <br> (Default: $H_i^{*,l}\left(T,p\right) - H_i^{*,l}\left(T, p_i^{*,l}\right)$ $= 0$) |
| $H_i^{*,l}\left(T,p\right) -$ $H_i^{*,l}\left(T, p_i^{*,l}\right)$ <br><br> DHLPC | Subord. | 1 | $\left( H_i^{*,l}\left(T,p\right) - H_i^{*,ig}\left(T\right) \right) -$ $\left( H_i^{*,l}\left(T, p_{pi}^{*,l}\right) - H_i^{*,ig}\left(T\right) \right)$ | $p_i^{*,l}$ Model name <br> $\left( H_i^{*,l} - H_i^{*,ig} \right)$ Route ID |
| | | 2 | $\displaystyle\int_{p_i}^{p} \left[ V_i^{*,l} - T \left( \dfrac{\partial V_i^{*,l}}{\partial T} \right)_p \right] dp$ | $p_i^{*,l}$ Model name |

*Continued*

### *Liquid Enthalpy Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | | | $V_i^{*,l}$ Model name<br>Integration option code<br>(Default: 1 point ) |
| | | 3 | Specified model | $\left( H_i^{*,l}(T, p) - H_i^{*,l}(T, \right.$<br>Model name |
| $H_m^l$<br>HLMX | Major | 1 | Specified model | $H_m^l$ Model name |
| | | 2 | $\displaystyle\sum_i x_i H_i^{*,l} + H_m^{E,l}$ | $H_i^{*,l}$ Route ID<br>$H_i^{E,l}$ Route ID<br>(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<br>$x^t$ Route ID |
| $H_m^l - H_m^{ig}$<br>DHLMX | Subord. | 1 | Specified model | $\left( H_m^l - H_m^{ig} \right)$ Model name |
| | | 2 | $\displaystyle\sum_i x_i \left( H_i^{*,l} - H_i^{*,ig} \right) + H_m^{E,I}$ | $\left( H_i^{*,l} - H_i^{*,ig} \right)$ Route ID<br>$H_m^{E,l}$ Route ID<br>(Default: $H_m^{E,l}$ = 0 ) |

*Continued*

## *Liquid Enthalpy Methods (continued)*

| | | | | |
|---|---|---|---|---|
| | | 3 | Unsymmetric convention For subcritical components A or B: $$\sum_i x_A\left(H_A^{*,l} - H_A^{*,ig}\right) + H_m^{E,l}$$ $$H_m^{E,l} = -RT^2 \sum_B x_B\left(\frac{\delta \ln \gamma_B}{\gamma T}\right)$$ For supercritical component i or j: $$-RT^2 \sum_j x_j\left(\frac{\delta \ln \varphi_j^l}{\delta T}\right)$$ where: $$\varphi_\iota^l = \gamma_i\left(\frac{H_i}{p\gamma_i^\infty}\right)$$ $$\ln\left(\frac{H_i}{\gamma_\iota^\infty}\right) = \sum B\omega_B \ln\left(\frac{H_{iB}}{\gamma_{\iota B}^\infty}\right)$$ $$\ln = \lim_{\sum_i x_i \to 0}\left(\ln \gamma_\iota\right)$$ $$\sum_B w_B = 1$$ | $\left(H_A^{*,l} - H_A^{*,ig}\right)$ Route ID where: $\gamma_B$ Model name $H_{iB}$ 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 | $$H_m^{E,l} = -RT^2 \sum_i x_i\left(\frac{\partial \ln \gamma_i}{\partial T}\right)$$ | $\gamma_i$ Model name |

## Solid Enthalpy Methods

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $H_i^{*,s}$<br>HL | 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 |
| $H_i^{*,s} - H_i^{*,ig}$<br><br>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<br>$\left( H_i^{*,v} - H_i^{*,ig} \right)$ Route ID<br>(Default: $H_i^{*,v} - H_i^{*,ig} = 0$)<br>$\Delta_{sub}H_i^{*}(T)$ Model name<br>$\left( H_i^{*,s}(T,p) - H_i^{*,s}\left(T, p_i^{*,s}\right) \right)$<br>Route ID<br>  (Default:<br>$H_i^{*,s}(T,p) - H_i^{*,s}\left(T, p_i^{*,s}\right) = 0$) |
| $H_i^{*,s}(T,p) - H_i^{*,s}$<br>DHSPC | Subord. | 1 | $\int_p^p \left[ V_i^{*,s} - T\left( \frac{\partial V_i^{*,s}}{\partial T} \right) \right] dp$ | $p_i^{*,s}$ Model name<br>$V_i^{*,s}$ Model name<br>Integration option code<br>(Default: 1 point) |
| $H_m^{s}$<br>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<br>$H_i^{*,s}$ Route ID<br>$H_m^{E,s}$<br>(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 |
| $H_m^{s} - H_m^{ig}$<br>DHSMX | Subord. | 1 | Specified model | $\left( H_m^{s} - H_m^{ig} \right)$ Model name |

*Continued*

## Solid Enthalpy Methods (continued)

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | 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<br><br>$H_m^{E,s}$ Route ID<br><br>(Default: $H_m^{E,s} = 0$ ) |
| $H_m^{E,s}$<br>HSXS | Subord. | 1 | Specified model | $H_m^{E,s}$ Model name |
| | | 2 | $H_m^{E,s} = -RT^2 \sum_i x_i^s \left( \dfrac{\partial \ln \gamma_i^s}{\partial T} \right)$ | $\gamma_i$ Model name |

## Vapor Gibbs Energy Methods

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $\mu_i^{*,v}$<br>GV | Major | 1 | Specified model | $\mu_i^{*,v}$ Model name |
| | | 2 | $\mu_i^{*,ig} + \left( \mu_i^{*,v} - \mu_i^{*,ig} \right)$ | $\left( \mu_i^{*,v} - \mu_i^{*,ig} \right)$ Route ID<br><br>(Default: $\mu_i^{*,v} - \mu_i^{*,ig} = 0$ ) |
| $\mu_i^{*,v} - \mu_i^{*,ig}$<br><br>DGV | Subord. | 1 | Specified model | $\left( \mu_i^{*,v} - \mu_i^{*,ig} \right)$ Model name |
| | | 2 | $RT \ln \varphi_i^{*,v} + RT \ln \left( \dfrac{p}{p^{ref}} \right)$ | $\varphi_i^{*,v}$ Route ID |
| $G_m^v$<br>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 |

*Continued*

### *Vapor Gibbs Energy Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | 3 | $G_m^{ig} + \left( G_m^v - G_m^{ig} \right)$ | $\left( G_m^v - G_m^{ig} \right)$ Route ID <br><br> (Default: $G_m^v - G_m^{ig} = 0$) |
| $G_m^v - G_m^{ig}$ <br> DGVMX | Subord. | 1 | Specified model | $\left( G_m^v - G_m^{ig} \right)$ Model name |
| | | 2 | $RT \sum_i y_i \ln \varphi_i^v + RT \ln \left( \dfrac{p}{p^{ref}} \right)$ | $\varphi_i^{*,v}$ Route ID <br> (Default: $\varphi_i^{*,v} = 1$) |

### *Liquid Gibbs Energy Methods*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $\mu_i^{*,l}$ <br> 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 |
| $\mu_i^{*,l} - \mu_i^{*,ig}$ <br> 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 | $\left( \mu_i^{*,l}\left(T, p_i^{*,l}\right) - \mu_i^{*,ig}(T) \right) +$ <br> $\left( \mu_i^{*,l}(T, p) - \mu_i^{*,l}\left(T, p_i^{*,l}\right) \right)$ | $p_i^{*,l}$ Model name <br> $\left( \mu_i^{*,l} - \mu_i^{*,ig} \right)$ Route ID <br> (Default: $\mu_i^{*,l} - \mu_i^{*,ig} = 0$) <br> $\left( \mu_i^{*,l}(T, p) - \mu_i^{*,l}\left(T, p_i^{*,l}\right) \right)$ Route ID <br> (Default: $\mu_i^{*,l}(T, p) - \mu_i^{*,l}\left(T, p_i^{*,l}\right) = 0$) |

*Continued*

## *Liquid Gibbs Energy Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $\mu_i^{*,l}(T,p)-$ $\mu_i^{*,l}(T,p_i^{*,l})$ DGLPC | Subord. | 1 | $\left(\mu^{*,l}(T,p)-\mu_i^{*,ig}(T)\right)-$ $\left(\mu_i^{*,l}(T,p_i^{*,l})-\mu_i^{*,ig}(T)\right)$ | $p_i^{*,l}$ 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 | $\displaystyle\sum_i x_i\mu_i^{*,l} + RT\sum_i x_i \ln x_i + G_m^{E,l}$ | $\mu_i^{*,l}$ 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 | Electrolyte model $\left(x^t\right)$ | Model name $x^t$ Route ID |
| $G_m^l - G_m^{ig}$ D GLMX | 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: $G_m^{E,l}=0$) |
| $G_m^{E,l}$ GLXS | Subord. | 1 | Specified model | $G_m^{E,l}$ Model name |
| | | 2 | $\displaystyle RT\sum_i x_i \ln\gamma_i$ | $\gamma_i$ Model name |

## Solid Gibbs Energy Methods

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $\mu_i^{*,s}$ <br> GL | Major | 1 | Specified model | $\mu_i^{*,s}$ Model name |
| | | 2 | $\mu_i^{*,ig} + \left(\mu_i^{*,s} - \mu_i^{*,ig}\right)$ | $\left(\mu_i^{*,s} - \mu_i^{*,ig}\right)$ Route ID |
| $\mu_i^{*,s} - \mu_i^{*,ig}$ <br><br> DGL | Subord. | 1 | Specified model | $\left(\mu_i^{*,s} - \mu_i^{*,ig}\right)$ Model name |
| | | 2 | $RT\ln\varphi^{*,s} + RT\ln\left(\dfrac{p}{p^{ref}}\right)$ | $\varphi_i^{*,s}$ Route ID |
| | | 3 | $\left(\mu_i^{*,s}\left(T,p_i^{*,s}\right) - \mu_i^{*,ig}(T)\right) +$ <br> $\left(\mu_i^{*,s}(T,p) - \mu_i^{*,s}\left(T,p_i^{*,s}\right)\right)$ | $p_i^{*,s}$ Model name <br> $\left(\mu_i^{*,s}\left(T,p_i^{*,s}\right) - \mu_i^{*,ig}(T)\right)$ <br> Route ID <br> (Default: <br> $\mu_i^{*,l}\left(T,p_i^{*,s}\right) - \mu_i^{*,ig}(T) =$ 0) <br> $\left(\mu_i^{*,s}(T,p) - \mu_i^{*,s}\left(T,p_i^{*,s}\right)\right)$ <br> Route ID <br> (Default: <br> $\mu_i^{*,s}(T,p) - \mu_i^{*,s}\left(T,p_i^{*,s}\right) =$ 0 ) |
| $\mu_i^{*,s}(T,p) -$ <br> $\mu_i^{*,s}\left(T,p_i^{*,s}\right)$ <br><br> DGLPC | Subord. | 1 | $\displaystyle\int_{p_i^{*,l}}^{p} V_i^{*,l}\,dp$ | $p_i^{*,l}$ Model name <br> $V_i^{*,l}$ Model Name <br> Integration option code <br> (Default: 1 point) |
| $G_m^s$ <br> GLMX | Major | 1 | Specified model | $G_m^s$ Model name |
| | | 2 | $\displaystyle\sum_i x_i^s \mu_i^{*,s} + G_m^{E,s} + RT\sum_i x_i^s \ln\mu_i^{*,s}$ | Route ID <br><br> $G_m^{E,s}$ Route ID <br><br> (Default: $G_m^{E,s} = 0$ ) |

*Continued*

## *Solid Gibbs Energy Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | 3 | $G_m^{ig} + \left( G_m^{s} - G_m^{ig} \right)$ | |
| $G_m^{s} - G_m^{ig}$ <br> DGLMX | Subord. | 1 | Specified model | $\left( G_m^{s} - G_m^{ig} \right)$ Model name |
| | | 2 | $\sum_i x_i^{s} \left( \mu_i^{*,s} - \mu_i^{*,ig} \right) + G_m^{E,s}$ | $\left( \mu_i^{*,s} - \mu_i^{*,ig} \right)$ Route ID <br><br> $G_m^{E,s}$ Route ID <br><br> (Default: $G_m^{E,s} = 0$) |
| $G_m^{E,s}$ <br> GLXS | Subord. | 1 | Specified model | $G_m^{E,s}$ Model name |
| | | 2 | $RT \sum_i x_i^{s} \ln \gamma_i^{s}$ | $\gamma_i$ Model name |

## Vapor Entropy Methods

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $S_i^{*,v}$ <br> 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 <br> (Default: $S_i^{*,v} - S_i^{*,ig} = 0$) |
| | | 3 | Specified model | $S_i^{*,v}$ Model name |
| $S_i^{*,v} - S_i^{*,ig}$ <br><br> 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 <br> (Default: $H_i^{*,v} - H_i^{*,ig} = 0$) <br> $\left(\mu_i^{*,v} - \mu_i^{*,ig}\right)$ Route ID <br> (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 |
| $S_m^{v}$ | Major | 1 | $\dfrac{1}{T}\left(H_m^{v} - G_m^{v}\right)$ | $H_m^{v}$ Route ID <br> $G_m^{v}$ Route ID |
| | | 2 | $S_m^{ig} + \left(S_m^{v} - S_m^{ig}\right)$ | $\left(S_m^{v} - S_m^{ig}\right)$ Route ID <br> (Default: $S_m^{v} - S_m^{ig} = 0$) |
| | | 3 | Specified model | $S_m^{v}$ Model name |
| $S_m^{v} - S_m^{ig}$ <br><br> 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 <br> (Default: $H_m^{v} - H_m^{ig} = 0$) <br> $\left(G_m^{v} - G_m^{ig}\right)$ Route ID <br> (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 |

## *Liquid Entropy Methods*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $S_i^{*,l}$ <br> SL | Major | 1 | $$\frac{1}{T}\left(H_i^{*,l} - \mu_i^{*,l}\right)$$ | $H_i^{*,l}$ Route ID <br><br> $\mu_i^{*,l}$ 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 |
| $S_i^{*,l} - S_i^{*,ig}$ <br><br> DSL | Subord. | 1 | $$\left(\frac{H_i^{*,l} - H_i^{*,ig}}{T}\right) - \left(\frac{\mu_i^{*,l} - \mu_i^{*,ig}}{T}\right)$$ | $\left(H_i^{*,l} - H_i^{*,ig}\right)$ Route ID |
| | | 2 | $$-\frac{\partial}{\partial T}\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$$ | $\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$ Route ID <br><br> $\left(\mu_i^{*,l} - \mu_i^{*,ig}\right)$ Model name |
| | | 3 | Specified Model | $\left(S_i^{*,l} - S_i^{*,ig}\right)$ Model name |
| $S_m^l$ <br> SLMX | Major | 1 | $$\frac{1}{T}\left(H_m^l - G_m^l\right)$$ | $H_m^l$ Route ID <br> $G_m^l$ 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 <br> $G_m^l$ model <br> $x^t$ Route ID |
| $S_m^l - S_m^{ig}$ <br><br> DSLMX | Subord. | 1 | Specified model | $\left(S_m^l - S_m^{ig}\right)$ Model name |
| | | 2 | $$\left(\frac{H_m^l - H_m^{ig}}{T}\right) - \left(\frac{G_m^l - G_m^{ig}}{T}\right)$$ | $\left(H_m^l - H_m^{ig}\right)$ Route ID <br> $\left(G_m^l - G_m^{ig}\right)$ Route ID |
| | | 3 | $$-\frac{\partial}{\partial T}\left(G_m^l - G_m^{ig}\right)$$ | $\left(G_m^l - G_m^{ig}\right)$ Model name |

## *Solid Entropy Methods*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $S_i^{*,s}$ <br> 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 <br><br> $\mu_i^{*,s}$ Route ID |
| $S_i^{*,s} - S_i^{*,ig}$ <br><br> 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 <br><br> $\left(\mu_i^{*,s} - \mu_i^{*,ig}\right)$ Route ID |
| | | 2 | Specified model | $\left(S_i^{*,s} - S_i^{*,ig}\right)$ Model name |
| $S_m^s$ <br><br> SSMX | Major | 1 | $\dfrac{1}{T}\left(H_m^s - G_m^s\right)$ | $H_m^s$ Route ID <br> $G_m^s$ Route ID |
| | | 2 | $S_m^{ig} + \left(S_m^s - S_m^{ig}\right)$ | $\left(S_m^s - S_m^{ig}\right)$ Route ID |
| $S_m^s - S_m^{ig}$ <br> 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 <br><br> $\left(G_m^s - G_m^{ig}\right)$ 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 |
|---|---|---|---|---|
| $V_i^{*,v}$ <br> VV | Major | 1 | Specified model | $V_i^{*,v}$ Model name |
| $V_m^v$ <br> 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 <br> $V_m^v$ Model name |
| | | 3 | $V_m^v = f\left(\gamma_i\right)$ | $\gamma_i$ Model name <br> $V_m^v$ Model name (eos only) |
| $V_i^{*,l}$ <br> VL | Major | 1 | Specified model | $V_i^{*,l}$ Model name |
| $V_m^l$ <br> 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 <br> $V_m^l$ Model name |
| | | 3 | Electrolyte model $\left(x^t\right)$ | $V_i^{*,l}$ Model name <br> $x^t$ Route ID |
| | | 4 | $V_m^l = f\left(\gamma_i\right)$ | $\gamma_i$ Model name <br> $V_m^l$ Model name (eos only) |
| $V_i^{*,s}$ <br> VS | Major | 1 | Specified model | $V_i^{*,s}$ Model name |
| $V_m^s$ <br> 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 <br> $V_m^s$ 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 | $\eta_i^{*,v} = \eta_i^{*,v}(p=0)$ | $\left(\eta_i^{*,v}(p=0)\right)$ Route ID |
| | | 3 | $\eta_i^{*,v} = f\left(V_i^{*,v}\right)$ | $V_i^{*,v}$ Route ID $\eta_i^{*,v}$ Model name |
| | | 4 | $\eta_i^{*,v} = \eta_i^{*,v}(p=0)$ $\quad + \left(\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0)\right)$ | $\left(\eta_i^{*,v}(p=0)\right)$ Route ID $\left(\eta_i^{*,v}(p) - \eta_i^{*,v}(p=0)\right)$ Route ID |
| $\eta_i^{*,v}(p=0)$ MUVLP | Subord. | 1 | Specified model | $\left(\eta_i^{*,v}(p=0)\right)$ Model name |
| $\begin{pmatrix} \eta_i^{*,v}(p) - \\ \eta_i^{*,v}(p=0) \end{pmatrix}$ MUVPC | Subord. | 1 | Specified model | $\left(\eta_i^{*,v}(p) - \eta_o^{*,v}(p=0)\right)$ 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 | $\eta^v$ Model name |
| | | 2 | $\eta^v = f\left(y_i, \eta_i^{*,v}\right)$ | $\eta_i^{*,v}$ Route ID $\eta^v$ Model name |
| | | 3 | $\eta^v = \eta^v(p=0)$ | $\left(\eta^v(p=0)\right)$ 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) + $ $\quad \left(\eta_i^v(p) - \eta_i^v(p=0)\right)$ | $\eta^v$ Model name $\left(\eta^v(p=0)\right)$ Route ID $\left(\eta_i^v(p) - \eta_i^v(p=0)\right)$ Route ID |

*Continued*

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## *Viscosity Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $\left(\eta^v(p=0)\right)$ MUVMXLP | Subord. | 1 | Specified model | $\left(\eta^v(p=0)\right)$ Model name |
| | | 2 | $\left(\eta^v(p=0)\right) = f\left(y_i, \eta_i^{*,v}(p=0)\right)$ | $\left(\eta_i^{*,v}(p=0)\right)$ Route ID $\left(\eta^v(p=0)\right)$ Model name |
| $\begin{pmatrix}\eta^v(p) - \\ \eta^v(p=0)\end{pmatrix}$ 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 |
| $\eta^l$ MULMX | Major | 1 | Specified model | $\eta^l$ Model name |
| | | 2 | $\eta^l = f\left(x_i, \eta_i^{*,l}\right)$ | $\eta_i^{*,l}$ Route ID $\eta^l$ Model name |
| | | 3 | $\eta^l = f\left(V_m^l\right)$ | $V_m^l$ Route ID $\eta^l$ Model name |
| | | 4 | Electrolyte model $\left(x^t\right)$ | $\eta^l$ Model name $x^t$ Route ID |

## *Thermal Conductivity Methods*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $\lambda_i^{*,v}$ MUV | Major | 1 | Specified model | $\lambda_i^{*,v}$ Model name |
| | | 2 | $\lambda_i^{*,v} = \left(\lambda_i^{*,v}(p=0)\right)$ | $\left(\lambda_i^{*,v}(p=0)\right)$ Route ID |
| | | 3 | $\lambda_i^{*,v} = \lambda_i^{*,v}(p=0)$ $+\left(\lambda_i^{*,v}(p)-\lambda_i^{*,v}(p=0)\right)$ | $\left(\lambda_i^{*,v}(p=0)\right)$ Route ID $\left(\lambda_i^{*,v}(p)-\lambda_i^{*,v}(p=0)\right)$ 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 | $\left(\lambda_i^{*,v}(p)-\lambda_i^{*,v}(p=0)\right)$ 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 $\left(\lambda_i^{*,v}(p)-\lambda_i^{*,v}(p=0)\right)$ Model name |
| $\lambda^v$ KVMX | Major | 1 | Specified model | $\lambda^v$ Model name |
| | | 2 | $\lambda^v = f\left(y_i,\lambda_i^{*,v}\right)$ | $\lambda_i^{*,v}$ Route ID $\lambda^v$ Model name |
| | | 3 | $\lambda^v = \lambda^v(p=0)$ | $\left(\lambda^v(p=0)\right)$ Route ID |

*Continued*

## *Thermal Conductivity Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | 4 | $\lambda^v = \lambda^v(p=0) +$ $\left(\lambda^v(p) - \lambda^v(p=0)\right)$ | $\left(\lambda^v(p=0)\right)$ Route ID $\left(\lambda^v(p) - \lambda^v(p=0)\right)$ Route ID |
| | | 5 | $\lambda^v = f\left(V_m^v, \eta^v(p=0)\right)$ | $V_m^v$ Route ID $\left(\eta^v(p=0)\right)$ Route ID $\lambda^v$ Model name |
| $\lambda^v(p=0)$ KVMXLP | Subord. | 1 | Specified model | $\left(\lambda^v(p=0)\right)$ Model name |
| | | 2 | $\lambda^v(p=0) =$ $f\left(y_i, \lambda_i^{*,v}(p=0), \eta_i^{*,v}(p=0)\right)$ | $\lambda_i^{*,v}$ Route ID $\eta_i^{*,v}(p=0)$ Route ID $\left(\lambda^v(p=0)\right)$ Model name |
| $\lambda^v(p) - \lambda^v(p=0)$ KVMXPC | Subord. | 1 | Specified model | $\left(\lambda^v(p) - \lambda^v(p=0)\right)$ Model name |
| | | 2 | $\left(\lambda^v(p) - \lambda^v(p=0)\right) = f\left(V_m^v\right)$ | Route ID $\left(\lambda^v(p) - \lambda^v(p=0)\right)\left(\lambda^v(p) - \lambda^v(p\right.$ Model name |
| $\lambda_i^{*,l}$ KL | Major | 1 | Specified model | $\lambda_i^{*,l}$ Model name |
| | | 2 | $\lambda_i^{*,l} = f\left(V_i^{*,l}, \eta_i^{*,v}(p=0)\right)$ | $V_i^{*,l}$ Route ID $\left(\eta_i^{*,v}(p=0)\right)$ Route ID $\lambda_i^{*,l}$ Model name |
| $\lambda^l$ KLMX | Major | 1 | Specified model | $\lambda^l$ Model name |
| | | 2 | $\lambda^l = f\left(x_i, \lambda_i^{*,l}\right)$ | $\lambda_i^{*,l}$ Route ID $\lambda^l$ Model name |

*Continued*

### *Thermal Conductivity Methods (continued)*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | 3 | $\lambda^l = f\left(V_m^l, \eta^v\left(p=0\right)\right)$ | $V_m^l$ Route ID<br>$\left(\eta^v\left(p=0\right)\right)$ Route ID<br>$\lambda^l$ Model name |
| | | 4 | Electrolyte model $\left(x^t\right)$ | $\lambda^l$ Model name<br>$x^t$ Route ID |
| $\lambda_i^{*,s}$<br>KS | Major | 1 | Specified model | $\lambda_i^{*,s}$ Model name |
| $\lambda^s$<br>KSMX | Major | 1 | Specified model | $\lambda^s$ Model name |
| | | 2 | $\lambda^s = f\left(x_i^s, \lambda_i^{*,s}\right)$ | $\lambda_i^{*,s}$ Route ID<br>$\lambda^s$ Model name |

### *Diffusion Coefficient Methods*

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $D_{ij}^v$<br>DV | Major | 1 | Specified model | $D_{ij}^v$ Model name |
| $D_i^v$<br>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<br>$y_i$ Model name |
| $D_{ij}^l$<br>DL | Major | 1 | Specified model | Model name |
| $D_i^l$<br>DLMX | Major | 1 | Specified model | Model name |

*Continued*

### Diffusion Coefficient Methods (continued)

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| | | 2 | $D_i^l = f\left(x_i, D_{ij}^l\right)$ | $D_{ij}^l$ Route ID<br>$D_i^l$ Model name |
| | | 3 | $D_i^l = f\left(x_i, \eta^l\right)$ | $\eta^l$ Route ID<br>$D_i^l$ Model name |
| | | 4 | Electrolyte model $\left(x^t\right)$ | $D_i^l$ Model name<br>$x^t$ Route ID |

### Surface Tension Methods

| Property Symbol and Name | Property Type | Method Code | Method | Route Structure Information Required |
|---|---|---|---|---|
| $\sigma_i^{*,l}$<br>SIGL | Major | 1 | Specified model | Model name |
| $\sigma^l$<br>SIGLMX | Major | 1 | Specified model | Model name |
| | | 2 | $\sigma^l = f\left(x_i, \sigma_i^{*,l}\right)$ | $\sigma_i^{*,l}$ Route ID<br>$\sigma^l$ Model name |
| | | 3 | Electrolyte model $\left(x^t\right)$ | $\sigma^l$ Model name<br>$x^t$ 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, this chapter. (Example 1 discusses a route that does *not* depend on other routes.)

Each built-in route in Aspen Plus has a unique route ID, which is composed of the property name (see the tables labeled Major Properties in Aspen Plus, Subordinate Properties in Aspen Plus, and Intermediate Properties in Aspen Plus, all earlier in this chapter) 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 simulation.

A property method can calculate a fixed list of properties (see Physical Properties in Aspen Plus, this chapter). 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*

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### Example 1    Route information for PHILMX, method 1

The first method from the table labeled Liquid Fugacity Coefficient Methods, this
chapter, 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:

$$\varphi_i^l = f\left(p, T, x_i, correlation\ parameters\right)$$

There are many models that can be used to calculate $\varphi_i^l$, 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, this chapter) 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, Aspen Plus 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, this chapter, 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 on page 4-41, Transport Physical Property Models on page 4-43, and Nonconventional Solid Property Models on page 4-44. If you need to use a proprietary model or a new model from the literature, you can interface these to Aspen Plus (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 | [†,††] |

*Continued*

## *Thermodynamic Physical Property Models (continued)*

| Thermodynamic Properties Model | Model Name | Phase | Properties |
|---|---|---|---|
| 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 |

*Continued*

## *Thermodynamic Physical Property Models (continued)*

| Thermodynamic Properties Model | Model Name | Phase | Properties |
|---|---|---|---|
| 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 |
| 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<br>MUL0H2O | V<br>L | MUV<br>MUL |
| IAPS thermal conductivity | KV0H2O<br>KL0H2O | V<br>L | KV<br>KL |

*Continued*

## *Transport Property Models (continued)*

| Thermodynamic Properties Model | Model Name | Phase | Properties |
|---|---|---|---|
| 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<br>MUL0TRAP, MUL2TRAP | V<br>L | MUV, MUVMX,<br>MUL, MULMX |
| 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 |
| 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) |

*Continued*

## *Option Codes for Activity Coefficient Models (continued)*

| Model Name | Option Code | Value | Descriptions |
|---|---|---|---|
| | | 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 |

*Continued*

### Option Codes for Activity Coefficient Models (continued)

| Model Name | Option Code | Value | Descriptions |
|---|---|---|---|
| | | 0 | Standard electrolytes method (Pre release 10) |
| | | 1 | Helgeson method (default) |
| | 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 |

*Continued*

## *Option Codes for Equation of State Models (continued)*

| Model Name | Option Code | Value | Descriptions |
|---|---|---|---|
| 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 ** Tri) |
| ESRKSTD, ESRKSTD0 | 1 | 0 | ASPEN Boston/Mathias alpha function |
| | | 1 | Original literature alpha function (default) |
| | | 2 | Grabowski and Daubert alpha function for H2 above TC (alpha = 1.202 exp(-0.30228 ** 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 ** 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 |

*Continued*

## Option Codes for Equation of State Models (continued)

| Model Name | Option Code | Value | Descriptions |
|---|---|---|---|
| | | 0 | Estimate (default) |
| | | 1 | Set to zero |
| ESHF, ESHF0 | 1 | 0 | Equation form for Log(k) expression: LOG(K) = A + B/T + C**LN(T) + D**T (default) |
| | | 1 | LOG(K) = A + B/T + C**T + D/T^2 + E**LOG(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) |
| 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. The following example 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. Aspen Plus 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 Aspen Plus 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, this chapter, 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, this chapter.

# Modifying and Creating Property Method

The built-in property methods in Aspen Plus 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

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 chapter). 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,

    a.  Select the route, the click on the View button to get the tree diagram for this route (see Routes and Models, this chapter). You can now trace the route in detail.
    b)  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 based property method

The Poynting correction is the pressure correction to the pure component liquid fugacity coefficient. For validation purposes, you need to compare your simulation 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 chapter). 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, this chapter). 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, this chapter.)

   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, this chapter).

## 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 Aspen Plus 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    Using COSTALD liquid molar volume in PENG-ROB

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, Aspen Plus 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 simulations. One year later you may have a similar project where you begin with your old simulation 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.

    Aspen Plus 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, Aspen Plus 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 Aspen Plus cover most engineering needs (see Routes and Models, this chapter). However, while modifying or creating property methods you may need a route that is not built-in (see Modifying and Creating Property Methods, this chapter). 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, this chapter). 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      Use a second data set of NRTL parameters for HLXS

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 simulation.

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 Aspen Plus 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.

# 5 Electrolyte Simulation

Electrolyte process simulation has many applications. In Aspen Plus, 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 simulation with Aspen Plus 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 simulation 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 simulation 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 simulations 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 simulations 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, Aspen Plus bypasses all solution chemistry calculations for such systems.

If you define the reactions on the Reactions Chemistry form, Aspen Plus checks for infeasible or redundant reactions. If such reactions exist, Aspen Plus 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 simulation. 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. Aspen Plus 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 simulation, the true component approach requires that you specify the process in terms of true components. Aspen Plus 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 Aspen Plus 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, Aspen Plus uses one arbitrary solution of the amounts of apparent electrolytes:

$$n_{ca}^a = \frac{n_c^t n_a^t}{\sum_c z_c n_c^t} \tag{7}$$

This solution generates all possible combinations of anions and cations. However, for the case of 2-2 electrolytes, the amount is multiplied by 2, to avoid the creation of, for example, $(Ca_2SO_4)_2$ 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 simulation, 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 simulation. 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 $\beta$ 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 (Maurer, 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 simulation. 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 Plus 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, for details on data regression.

# References

L.A. Bromley, "Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions," *AIChE J.*, Vol. 18, (1973), p. 313.

C.C. Chen, H.I. Britt, J.F Boston, and L.B. Evans, "Local Composition Model for Excess Gibbs Energy of Electrolyte Systems," *AIChE J.*, Vol. 28, (1982), p. 588.

C.C. Chen, H.I. Britt, J.F. Boston, and W.M. Clarke, "Thermodynamic Property Evaluation in Computer-Based Flowsheet Simulation for Aqueous Electrolyte Systems," Paper presented at the Denver AIChE Meeting, August, 1983.

W. Fürst and H. Renon. "Representation of Excess Properties of Electrolyte Solutions Using a New Equation of State." *AIChE J.*, Vol. *39,* No. 2, (1993), pp. 335-343.

G., Mauer, "Electrolyte Solutions," *Fluid Phase Equilibria*, Vol. 13, (1983), p. 269.

H.P. Meissner and C.L. Kusik, "Aqueous Solutions of Two or More Strong Electrolytes-Vapor Pressures and Solubilities," *Ind. Eng. Chem. Process Res. Develop.*, Vol. 12, (1973), p. 205.

B. Mock, L.B. Evans, and C.-C. Chen, "Phase Equilibria in Multiple-Solvent Electrolyte Systems: A New Thermodynamic Model," Paper presented at the Boston Summer Computer Simulation Conference, July 1984.

Pitzer, K.S., "Thermodynamics of Electrolytes.I. Theoretical Basis and General Equations," *J. Phys. Chem.*, Vol. 77, (1973), p. 268.

H. Planche and H. Renon, "Mean Spherical Approximation Applied to a Simple but Nonprimitive Model of Interaction for Electrolyte Solutions and Polar Substance," *J. Phys. Chem*, Vol. 85, (1981), p. 3924.

H. Renon and J.M. Prausnitz, "Local Compositions in Thermodynamic Excess Function for Liquid Mixtures," *AIChE J.*, Vol. 14, (1968), p. 135.

S. Watanasiri, M.R. Brule, and L.L. Lee, "Prediction of Thermodynamic Properties of Electrolytic Solutions Using the Me an Spherical Approximation," *J. Phys. Chem.*, Vol. 86, (1982), p. 282.

# 6     Free-Water and Rigorous Three-Phase Calculations

This chapter describes free-water and rigorous three-phase calculations in Aspen Plus. Guidelines to help you choose the most appropriate method are included.

The following tablelists 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 | See footnote.[††] |

*Continued*

### Unit Operation Models That Allow Three-Phase Calculations

| Name | Description | Free-Water Calculations | Water Decant Stream | Rigorous Three-Phase Calculations |
|------|-------------|-------------------------|---------------------|-----------------------------------|
| 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 | See footnote.[††] |
| 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 on page 6-1 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, Aspen Plus places the water phase in the decant stream. If you do not specify a decant stream, Aspen Plus 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:

$$K_w^* = \varphi_w^{*,l} \Big/ \varphi_w^v$$

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)

$\varphi_w^v$ = 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:

$\gamma_w$ = 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

$\varphi_w^v$ = The fugacity coefficient of water in the vapor phase mixture, calculated using the primary property method

You can select the calculation methods for $\gamma_w$ and $\varphi_w^v$ using the Water solubility field on the Properties Specifications Global sheet or the Blockops form.

| Solu-water option | Calculate $\gamma_w$ from | Calculate $\varphi_w^v$ from |
|---|---|---|
| 0 | $$\gamma_w = \frac{1}{x_w^{sol}}$$ | Free-water property method |
| 1 | $$\gamma_w = \frac{1}{x_w^{sol}}$$ | Primary property method |
| 2 | $\gamma_w = f(T, x_w)$ where $\gamma_w = \dfrac{1}{x_w^{sol}}$ <br><br> 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 $i$th organic species

$x_{wi}^{sol}$    =    Mole fraction solubility of water in the $i$th species

The value of $x_{wi}^{sol}$ is calculated as a function of temperature, using the Water Solubility model (WATSOL).

# 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 on page 6-1. These calculations make no assumptions about the nature of the two liquid phases. Aspen Plus 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.

# 7    Petroleum Components Characterization Methods

Aspen Plus 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 Aspen Plus 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) |

*Continued*

## *Petroleum Components Characterization Methods (continued)*

| Parameter | Description | Model Available |
|---|---|---|
| PC | Critical pressure | Cavett (1962)<br>Kesler-Lee (1976)<br>Riazi API (1987)<br>Riazi-Daubert (1980)<br>Tsang-Aspen (1978)<br>Twu (1984) |
| VC | Critical volume | Brule et al. (1982)<br>Reidel (1954)<br>Twu (1984) |
| PL | Vapor pressure | BK-10<br>Kesler-Lee (1980)<br>Maxwell-Bonnell (1955)<br>Tsang-SWAP (1978) |
| CPIG | Ideal gas heat capacity | Brule et al. (1982)<br>Cavett (1962)<br>Kesler-Lee (1976)<br>Mathias-Monks (1982)<br>Tsang-Aspen (1978) |
| VL | Liquid molar volume | Cavett<br>Rackett (Spencer, 1972) |
| DHVL | Enthalpy of vaporization | Vetere (1973) |
| OMEGA | Acentric factor | Defining relation<br>Kesler-Lee (1976)<br>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<br>Montgomery (1988) |
| DGFORM | Standard Gibbs energy of formation | Default to zero<br>Montgomery (1988) |
| WATSOL | Water solubility in hydrocarbon | ASPEN PLUS<br>API Kerosene<br>Hibbard-Schalla |
| RKSKIJ | RKS binary parameters | API 1978<br>API 1987 |

# Property Methods for Characterization of Petroleum Components

Since there are several methods available for estimation of a given parameter, Aspen Plus 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 |
| $T_c$ | Riazi-Daubert |
| $P_c$ | Riazi-Daubert |
| $V_c$ | 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 Plus |
| 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 |
| $T_c$ | Riazi-Daubert |
| $P_c$ | Riazi-Daubert |
| $V_c$ | 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 Plus |
| Standard enthalpy of formation | Default to zero |
| Standard Gibbs energy of formation | Default to zero |
| Water solubility in hydrocarbon | Aspen Plus |
| 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. |

*Continued*

**Property Method API-METH: For COAL-LIQ; For Coal Liquids (continued)**

| | |
|---|---|
| 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 |
| $T_c$ | Kesler-Lee |
| $P_c$ | Kesler-Lee |
| $V_c$ | 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 Plus |
| 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 |
| $T_c$ | Twu |
| $P_c$ | Twu |
| $V_c$ | Twu |
| Vapor pressure | BK-10 |
| Ideal gas heat capacity | Kesler-Lee |
| Liquid molar volume | Rackett |
| Enthalpy of vaporization | Vetere |
| Acentric factor | Kesler-ASPEN |

*Continued*

**Property Method API-TWU: AspenTech, API, and Twu (continued)**

| Property | Method |
|---|---|
| Viscosity | Watson |
| Water solubility | API kerosene-line |
| Standard enthalpy of formation | Montgomery |
| Standard Gibbs energy of formation | Montgomery |
| RKS binary parameters | API 1978 |

# References

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

R.H. Cavett, "Physical Data for Distillation Calculations – Vapor-Liquid Equilibria," Presented at 27th Midyear Meeting of API Division of Refining, May 15, 1982.

R.H. Cavett, FLOWTRAN Physical Properties Reference Manual, Monsanto Company.

C.W. Edmister, e. Applied Hydrocarbon Thermodynamics, 2nd edition, Gulf Publishing Co., (1988).

O.H. Hariu and R.C. Sage, *Hydro. Proc.*, (1969).

M.G. Kesler and B.I. Lee, *Hydro. Proc.*, 55 (3), p. 153, (1976).

M.G. Kesler and B.I. Lee, *Hydro. Proc.*, 59 (7), p. 163, (1980).

P.M. Mathias, and K.G. Monks, SRC-I Quarterly Progress Report, Air Products and Chemicals, Inc., April – June 1982.

Maxwell and Bonnell, API Procedure 5A1.15.

L. Reidel, API Prodedure 4A3.1.

M.R. Riazi and T.E. Daubert, *Hydro. Proc.*, 59 (3), p. 115, (1980).

D. B. Robinson and D. Y. Peng "The Characterization of the Heptanes and Heavier Fractions for the GPA Peng-Robinson Programs," GPA Research Report RR-28, March (1978).

C.F. Spencer and R.P. Danner, *J. Chem Eng. Data.*, 17, (1972).

M. Tsang, Computer-Aided Industrial Process Design, The ASPEN Project, Second Annual Report, June 1, 1977 to May 30, 1978; Submitted to U.S. D.O.E. by M.I.T. Department of Chemical Engineering and Energy Laboratory under Contract No. E(49–18) 2295, Task No. 9, June 15, 1978.

A. Vetere, "Modification of the Kistiakowsky Equation for the Calculation of the Enthalpies of Vaporization of Pure Compounds," Laboratory Richerche Chimica Industriale SNAM PROGETTI, San Donato, Milanese, 1973.

K. Watson et al., API Figure 11A4.1.

C. H. Twu, Fluid Phase Equilibria, 16, p. 137 (1984).

# 8 Property Parameter Estimation

This chapter describes:

- Estimation methods used by the Property Constant Estimation System (PCES)
- How to generate a report for the estimated parameters

If you request estimation, Aspen Plus, 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 lists all the parameters that Aspen Plus can estimate.

### *Parameters Estimated by Aspen Plus*

**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 | |
| VB | Liquid molar volume at TB | |

*Continued*

**Pure Component Constants (continued)**

| Parameter | Description | Model |
|-----------|-------------|-------|
| 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.*

[††]   *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, Aspen Plus 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 Plus databank.

## Normal Boiling Point (TB)

Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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, *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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, *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus Physical Property Data* lists the functional groups for this method.

# Critical Compressibility Factor (ZC)

Aspen Plus calculates the critical compressibility factor (ZC) by:

$$Z_c = \frac{P_c V_c}{R T_c}$$

Where:

| | | |
|---|---|---|
| $R$ | = | Universal gas constant |
| $P_c$ | = | Critical pressure |
| $V_c$ | = | Critical volume |
| $T_c$ | = | Critical temperature |

# 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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. Aspen Plus does not generate this information automatically from the general molecular structure.

Table 3.2 in *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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 *Aspen Plus 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:

$$DGAQHG = \frac{\left(DHAQFM + 12822.8\right)}{1.105}$$

### 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:

$$DGAQHG = 122110.2752 + 2839.2534 * \left(S025C - S025E\right)$$

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. Aspen Plus 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 *Aspen Plus Physical Property Data* lists the functional groups for the Bondi method.

# A      Bromley-Pitzer Activity Coefficient Model

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):

$$\frac{G^E}{RT} = n_W \left[ f(I) + \sum_i \sum_j B_{ij} m_i m_j + \sum_i \sum_j \theta_{ij} m_i m_j + \frac{1}{2} \sum_i \sum_j \left( \sum_k m_k z_k \right) C_{ij} m_i m_j + \frac{1}{6} \sum_i \sum_j \sum_k \psi_{ijk} m_i m_j m_k \right]$$

(1)

Where:

| | | |
|---|---|---|
| $G^E$ | = | Excess Gibbs energy |
| $R$ | = | Gas constant |
| $T$ | = | Temperature |
| $n_w$ | = | Kilograms of water |
| $z_i$ | = | Charge number of ion $i$ |

$$m_i = \frac{x_i}{x_w}\left(\frac{M_w}{1000}\right) = \frac{n_i}{n_w} = \text{ molality of ion } i$$

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 $i$

$B$, $C$, $\theta$ and $\psi$ 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 $\psi$ 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, $\beta$ 's and $\theta$ '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, $\beta_{ion}$ and $\delta_{ion}$ (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.

# Parameter Conversion

For 2-2 electrolytes, the parameter $\beta^{(3)}$ corresponds to Pitzer's $\beta^{(1)}$; $\beta^{(2)}$ is the same in both Aspen Plus 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 Plus $\beta^{(3)}$ Be careful to make this distinction when entering 2-2 electrolyte parameters.

(L.A. Bromley).

(Fürst and H. Renon).

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.

| Bromley-Pitzer Activity Coefficient Model | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | |

# B Electrolyte NRTL Activity Coefficient Model

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 coefficents 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 $\gamma$, 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

$A_\varphi$ = Debije-Hückel parameter:

$$A_\varphi = \frac{1}{3}\left(\frac{2\pi N_A d}{1000}\right)^{1/2}\left(\frac{Q_e^2}{\varepsilon_w kT}\right)^{3/2} \tag{4}$$

$N_A$ = Avogadro's number

$d$ = Density of solvent

$Q_e$ = Electron charge

$\varepsilon_w$ = Dielectric constant of water

$T$ = Temperature

$k$ = Boltzmann constant

$I_x$ = Ionic strength (mole fraction scale):

$$I_x = \frac{1}{2}\sum_i x_i z_i^2 \tag{5}$$

$x_i$ = Mole fraction of component $i$

$z_i$ = Charge number of ion $i$

$\rho$ = "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:

$r_i$     =     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:

$X_j$     =     $x_j C_j$ ( $C_j = z_j$ for ions and $C_j$ = unity for molecules)

$G_{ji}$     =     $e^{\left(-\alpha_{ji}\tau_{ji}\right)}$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$$

$$\alpha_{ji} = \text{Nonrandomness factor}$$

$g_{ji}$ and $g_{ii}$ are energies of interaction between species $j$ and $i$, and $i$ and $i$, respectively. Both $g_{ij}$ and $\alpha_{ij}$ 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:

$$G_{ji,ki} = e^{\left(-\alpha_{ji,ki}\tau_{ji,ki}\right)}$$

$$\tau_{ji,ki} = \frac{g_{ji} - g_{ki}}{RT}$$

$$\alpha_{ji,ki} = \text{Nonrandomness factor}$$

# 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          cation at          anion at
center              center             center
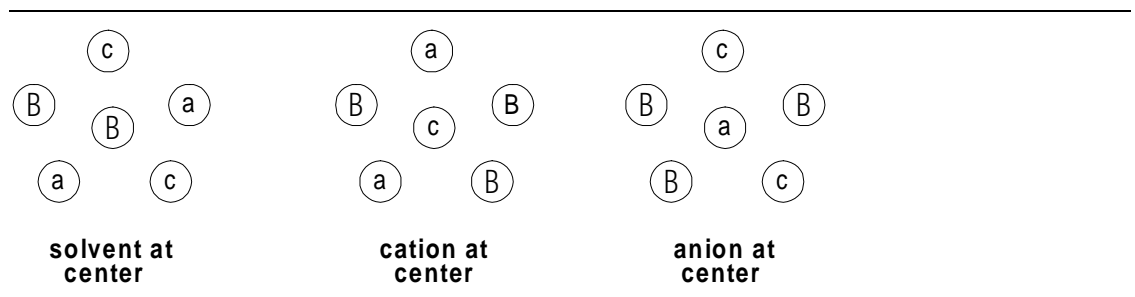
In the case of a central solvent molecule with other solvent molecules, cations, and anions in its immediate neighborhood, the principle of local electroneutrality is followed: the surrounding cations and anions are such that the neighborhood of the solvent is electrically neutral. In the case of a central 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.

$$X_{iB} = \frac{X_i G_{iB}}{X_a G_{cB} + X_c G_{cB} + X_B G_{BB}} \qquad i = c,\ a,\ or\ B \tag{14}$$

$$X_{ac} = \frac{X_a}{X_a + X_B G_{Bc,ac}} \tag{15}$$

$$X_{ca} = \frac{X_c}{X_c + X_B G_{Ba,ca}} \tag{16}$$

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

$z_a$     =     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:

$$G_m^{E,lc} = x_m\left(G_m(B-cell) - G_m^{ref}(B-cell)\right) + x_c\left(G_m(c-cell) - G_m^{ref}(c-cell)\right) \\ + x_a\left(G_m(a-cell) - G_m^{ref}(a-cell)\right) \tag{23}$$

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:

$$\frac{G_m^{E,lc}}{RT} = X_B X_{cB}\tau_{cB} + X_B X_{aB}\tau_{aB} + X_c X_{Bc} z_c \tau_{Bc,ac} + X_a X_{Ba} z_a \tau_{Ba,ca} \tag{24}$$

The assumption of local electroneutrality applied to cells with central solvent molecules may be stated as:

$$X_{aB} = X_{cB} \tag{25}$$

Combining this expression with the expression for the effective local mole fractions given in equations 9 and 10, the following equality is obtained:

$$G_{aB} = G_{cB} \tag{26}$$

The following relationships are further assumed for nonrandomness factors:

$$\alpha_{aB} = \alpha_{cB} = \alpha_{ca,B} \tag{27}$$

$$\alpha_{Bc,ac} = \alpha_{Ba,ca} = \alpha_{B,ca} \tag{28}$$

and,

$$\alpha_{ca,B} = \alpha_{B,ca} \tag{29}$$

It can be inferred from equations 9, 10, and 26 to 29 that:

$$\tau_{aB} = \tau_{cB} = \tau_{ca,B} \tag{30}$$

$$\tau_{Bc,ac} = \tau_{Ba,ca} = \tau_{B,ca} \tag{31}$$

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.

$$\frac{1}{z_c} \ln \gamma_c^{*lc} = \frac{X_B^2 \tau_{cB} G_{cB}}{\left( X_c G_{cB} + X_a G_{aB} + X_B \right)^2} + \frac{X_a \tau_{Ba} X_B G_{Ba}}{\left( X_c + X_B G_{Ba} \right)^2}$$
$$+ \frac{X_B \tau_{Bc} G_{Bc}}{\left( X_a + X_B G_{Bc} \right)} - \tau_{Bc} - G_{cB} \tau_{cB} \tag{34}$$

$$\frac{1}{z_a} \ln \gamma_a^{*lc} = \frac{X_B^2 \tau_{aB} G_{aB}}{\left( X_c G_{cB} + X_a G_{aB} + X_B \right)^2} + \frac{X_c \tau_{Bc} X_B G_{Bc}}{\left( X_a + X_B G_{Bc} \right)^2}$$
$$+ \frac{X_B \tau_{Ba} G_{Ba}}{\left( X_c + X_B G_{Ba} \right)} - \tau_{Ba} - G_{aB} \tau_{aB} \tag{35}$$

$$\ln \gamma_B^{lc} = X_{cB} \tau_{cB} + X_{aB} \tau_{aB} + \frac{X_c G_{Bc} \tau_B X_a}{\left( X_a + G_{Bc} X_B \right)^2} + \frac{X_a G_{Ba} \tau_{Ba} X_c}{\left( X_c + G_{Ba} X_B \right)^2}$$
$$- \frac{X_c X_B G_{cB} \tau_{cB}}{\left( X_c G_{cB} + X_a G_{aB} + X_B \right)^2} - \frac{X_a X_B G_{aB} \tau_{aB}}{\left( X_c G_{cB} + X_a G_{aB} + X_B \right)^2} \tag{36}$$

# Multicomponent Systems

The Electrolyte NRTL model can be extended to handle multicomponent systems.

The excess Gibbs energy expression is:

$$
\frac{G_m^{E,lc}}{RT} = \sum_B X_B \frac{\sum_j X_j G_{jB} \tau_{jB}}{\sum_k X_k G_{kB}} + \sum_c X_c \sum_{a'} \left( \frac{X_a}{\sum_{a''} X_{a''}} \right) \frac{\sum_j X_j G_{jc,a'c} \tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}}
$$

$$
+ \sum_a X_a \sum_{c'} \left( \frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{\sum_j X_j G_{ja,c'a} \tau_{ja,c'a}}{\sum_k X_k G_{ka,c'a}}
$$

(37)

Where:

$j$ and $k$ can be any species ($a$, $C$, or $B$)

The activity coefficient equation for molecular components is given by:

$$
\ln \gamma_B^{lc} = \frac{\sum_j X_j G_{jB} \tau_{jB}}{\sum_k X_k G_{kB}} + \sum_{B'} \frac{X_{B'} G_{BB'}}{\sum_k X_k G_{kB'}} \left( \tau_{BB'} - \frac{\sum_k X_k G_{kB'} \tau_{kB'}}{\sum_k X_k G_{kB'}} \right)
$$

$$
+ \sum_c \sum_{a'} \frac{X_a}{\sum_{a''} X_{a''}} \frac{X_c G_{Bc,a'c}}{\sum_k X_k G_{kc,a'c}} \left( \tau_{Bc,a'c} - \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right)
$$

(38)

$$
+ \sum_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{X_a G_{Ba,c'a}}{\sum_k X_k G_{ka,c'a}} \left( \tau_{Bc,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right)
$$

The activity coefficient equation for cations is given by:

$$
\frac{1}{z_c} \ln \gamma_c^{lc} = \sum_{a'} \left( \frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} + \sum_{B'} \frac{X_B G_{cB}}{\sum_k X_k G_{kB}} \left( \tau_{cB} - \frac{\sum_k X_k G_{kB} \tau_{kB}}{\sum_k X_k G_{kB}} \right)
$$

$$
+ \sum_a \sum_{c'} \left( \frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{X_a G_{ca,c'a}}{\sum_k X_k G_{ka,c'a}} \left( \tau_{ca,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right)
$$

(39)

The activity coefficient equation for anions is given by:

$$\frac{1}{z_a}\ln\gamma_a^{lc} = \sum_{c'}\left(\frac{X_{c'}}{\sum_{c''}X_{c''}}\right)\frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} + \sum_B \frac{X_{Bm}G_{aB}}{\sum_k X_k G_{kB}}\left(\tau_{aB} - \frac{\sum_k X_k G_{k\mathbf{B}}\tau_{kB}}{\sum_k X_k G_{k\mathbf{B}}}\right)$$

$$+ \sum_c\sum_{a'}\left(\frac{X_{a'}}{\sum_{a''}X_{a''}}\right)\frac{X_c G_{ac,a'c}}{\sum_k X_k G_{kc,a'c}}\left(\tau_{ac,a'c} - \frac{\sum_k X_k G_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}}\right) \tag{40}$$

Where:

$$G_{cB} = \frac{\sum_a X_a G_{ca,B}}{\sum_{a'}X_{a'}} \tag{41}$$

$$G_{aB} = \frac{\sum_c X_c G_{ca,B}}{\sum_{c'}X_{c'}} \tag{42}$$

$$\alpha_{Bc} = \alpha_{cB} = \frac{\sum_a X_a \alpha_{B,ca}}{\sum_{a'}X_{a'}} \tag{43}$$

$$\alpha_{Ba} = \alpha_{aB} = \frac{\sum_c X_c \alpha_{B,ca}}{\sum_{c'}X_{c'}} \tag{44}$$

$$\tau_{cB} = -\frac{\ln G_{cB}}{\alpha_{cB}} \tag{45}$$

$$\tau_{aB} = -\frac{\ln G_{aB}}{\alpha_{cB}} \tag{46}$$

$$\tau_{Ba,ca} = \tau_{aB} - \tau_{ca,B} + \tau_{B,ca} \tag{47}$$

$$\tau_{Bc,ac} = \tau_{cB} - \tau_{ca,B} + \tau_{B,ca} \tag{48}$$

# 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, $\alpha$, and energy parameters, $\tau$.

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. Simulation 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 Plus 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.

# C      Pitzer Activity Coefficient Model

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:

$$g_{ij}(r) = 1 - q_{ij}(r) + \frac{1}{2} q_{ij}^2(r) \tag{1}$$

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:

$$\frac{G^E}{n_w RT} = f(1) + \sum_i \sum_j \lambda_{ij}(I)m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \qquad (2)$$

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 $\lambda_{ij}$ are second virial coefficients that account for the short-range forces between solutes $i$ and $j$. The parameters $\mu_{ijk}$ account for the interactions between solutes, $i, j, k$. For ion-ion interactions, $\lambda_{ij}$ is a function of ionic strength. For molecule-ion or molecule-molecule interactions this ionic strength dependency is neglected. The dependence of $\mu_{ijk}$ on ionic strength is always neglected. The matrices $\lambda_{ij}$ and $\mu_{ijk}$ 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:

$$\frac{G^e}{RT} = n_w \left[ \begin{array}{l} f(I) + 2\sum_c \sum_a m_c m_a \left( B_{ca} + \left( \sum_c m_c |z_c| \right) C_{ca} \right) \\ + \sum_c \sum_{c'} m_c m_{c'} \left( \theta_{cc'} + \frac{\sum_a m_a \Psi_{cc'a}}{2} \right) + \sum_a \sum_{a'} m_a m_{a'} \left( \theta_{aa'} + \frac{\sum_c m_c \Psi_{caa'}}{2} \right) \end{array} \right] \quad (3)$$

$z_i$ = Charge of ion $i$

Subscripts $c$, $c'$, and $a$, $a'$ denote cations and anions of the solution. $B$, $C$, $\theta$, and $\Psi$ 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 $\theta$ and $\Psi$ 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 $NaCl + KCl + H_2 0$ or $NaCl + NaNO_3 + H_2 0$ (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:

$$\frac{G^E}{RT} = n_w \left[ \begin{array}{l} f(I) + \sum_i \sum_j B_{ij} m_i m_j + \sum_i \sum_j \theta_{ij} m_i m_j + \tfrac{1}{2} \sum_i \sum_j \left( \sum_k m_k |z_k| \right) C_{ij} m_i m_j \\ + \tfrac{1}{6} \sum_i \sum_j \sum_k \Psi_{ijk} m_i m_j m_k \end{array} \right] \qquad (4)$$

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 $B_{ij}$, $C_{ij}$, $\theta_{ij}$, and $\Psi_{ijk}$ 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 $\theta_{ij}$ 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.

$\Psi_{ijk}$ 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:

$$
\begin{aligned}
\ln \gamma^*_{m,i} &= \frac{\partial \left( \dfrac{G^E}{RT} \right)}{\partial n_i} \\
&= \tfrac{1}{2} z_i^2 f' + 2\sum_j m_j B_{ij} + \tfrac{1}{2} z_i^2 \sum_i \sum_k B_{ij'} m_j m_k \\
&\quad + 2\sum_j \theta_{ij} m_j + \tfrac{1}{2} |z_i| \sum_j \sum_k C_{jk} m_j m_k \\
&\quad + \sum_j \left( \sum_k m_k |z_k| \right) C_{ij} m_j + \tfrac{1}{2} \sum_j \sum_k \Psi_{ijk} m_j m_k
\end{aligned}
\tag{5}
$$

Where $\theta'$ 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:

$$\frac{1000}{M_w} \ln \gamma_{m,w} = f - If' - \sum_i \sum_j m_i m_j B_{ij} - \sum_i \sum_j B_{ij'} I - \sum_i \sum_j m_i m_j \theta_{ij}$$
$$- \sum_i \sum_j \Sigma_k m_k |z_k| m_i m_j C_{ij} - \tfrac{1}{3} \sum_i \sum_j \sum_k m_i m_j m_k \Psi_{ijk}$$

(6)

$f(I)$, the electrostatic term, is expressed as a function of ionic strength $I$:

$$f(I) = -A_\varphi \left( \frac{4I}{b} \right) \left[ \ln \left( 1 + bI^{1/2} \right) \right]$$

(7)

$I$, the ionic strength, is defined as:

$$I = \tfrac{1}{2} \sum_i m_i z_i^2$$

(8)

Taking the derivative of equation 7 with respect to $I$, gives:

$$f'(I) = \frac{df}{dI} = -2A_\varphi \left[ \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln \left( 1 + bI^{1/2} \right) \right]$$

(9)

So that:

$$f(I) = -A_\varphi \left( \frac{4I}{b} \right) \left[ \ln \left( 1 + bI^{1/2} \right) \right]$$

(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:

$$A_\varphi = \tfrac{1}{3} \left( \frac{2\pi N_A d_w}{1000} \right)^{1/2} \left( \frac{Q_e^2}{\varepsilon_B kT} \right)^{3/2}$$

(11)

Where:

| | | |
|---|---|---|
| $N_A$ | = | Avogadro's constant |
| $d_w$ | = | Water density |
| $\varepsilon_B$ | = | 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:

$$\begin{aligned} B' &= \frac{2\beta^{(2)}}{144I^2}\left[-1 + \left(1 + 12I^2 + 72I\right)e^{\left(-12I^{\frac{1}{2}}\right)}\right] \\ &+ \frac{2\beta^{(3)}}{(1.4)^2 I^2}\left[-1 + \left(1 + 1.4I^{\frac{1}{2}} + \frac{(1.4)^2 I}{2}\right)e^{\left(-1.4I^{\frac{1}{2}}\right)}\right] \end{aligned} \tag{15}$$

The parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$ and also $C$, $\theta$, and $\Psi$ can be found in Pitzer's articles (see References on page C-11).

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:

$\gamma_m$      =      Activity coefficient (molality scale)

$\gamma_x$      =      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 $\Psi_{ijk}$ are extended to molecule-molecule-molecule interactions. The following expressions relate $\Psi_{ijk}$ to Pitzer's original $\mu_{ijk}$:

$$\Psi_{iii} = 6\mu_{iii}$$

However, molecule-molecule interactions were not taken into account by Pitzer and coworkers. So $\mu_{iii}$ 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 Aspen Plus 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 $C^{\Phi}$, 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, $C^{\Phi}$. The parameter names in Aspen Plus 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 Plus 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 Aspen Plus. 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 $C^{\Phi}$ 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 Plus 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:

$$4/3 \beta^{(0)} = 0.4698$$

$$4/3 \beta^{(1)} = 2.242$$

$$\frac{2^{5/2}}{3} C^{\phi} = 0.00979$$

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 |

*Continued*

| Reference | Parameters available |
|---|---|
| (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 |

C.-C. Chen, H.I. Britt, J.I. Boston and L.B. Evans, "Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes," *AIChE.J.*, Vol. 25, (1979), pp. 820-831.

M. Conceicao, P. de Lima, and K.S. Pitzer, "Thermodynamics of Saturated Aqueous Solutions Including Mixtures of NaCl, KCl, and CsCl, "*J. Solution Chem,* Vol. 12, No. 3, (1983), pp. 171-185.

W. Fürst and H. Renon, "Effects 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.

E.A. Guggenheim, *Phil. Mag.*, Vol. 7, No. 19, (1935), p. 588.

E.A. Guggenheim and J.C. Turgeon, *Trans. Faraday Soc.,* Vol. 51, (1955), p. 747.

J.C. Peiper and K.S. Pitzer, "Thermodynamics of Aqueous Carbonate Solutions Including Mixtures of Sodium Carbonate, Bicarbonate, and Chloride," *J. Chem. Thermodynamics*, Vol. 14, (1982), pp. 613-638.

R.C. Phutela and K.S. Pitzer, "Thermodynamics of Aqueous Calcium Chloride," *J. Solution Chem.*, Vol. 12, No. 3, (1983), pp. 201-207.

K.S. Pitzer, "Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations, " *J. Phys. Chem.,* Vol. 77, No. 2, (1973), pp. 268-277.

K.S. Pitzer, *J. Solution Chem.,* Vol. 4, (1975), p. 249.

K.S. Pitzer, "Theory: Ion Interaction Approach," *Activity Coefficients in Electrolyte Solutions,* Pytkowicz, R. ed., Vol. I, (CRC Press Inc., Boca Raton, Florida, 1979).

K.S. Pitzer, "Fluids, Both Ionic and Non-Ionic, over Wide Ranges of Temperature and Composition," *J. Chen. Thermodynamics*, Vol. 21, (1989), pp. 1-17. (Seventh Rossini lecture of the commission on Thermodynamics of the IUPAC, Aug. 29, 1988, Prague, ex-Czechoslovakia).

K.S. Pitzer and J.J. Kim, "Thermodynamics of Electrolytes IV; Activity and Osmotic Coefficients for Mixed Electrolytes," *J.Am. Chem. Soc.*, Vol. 96 (1974), p. 5701.

K.S. Pitzer and G. Mayorga, "Thermodynamics of Electrolytes II; Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent," *J. Phys. Chem.,* Vol. 77, No. 19, (1973), pp. 2300-2308.

K.S. Pitzer and L.F. Silvester, "Thermodynamics of Electrolytes VI. Weak Electrolytes Including $H_3PO_4$," *J. Solution Chem.,* Vol. 5, (1976), p. 269.

K.S. Pitzer and G. Mayorga, *J. Phys Chem.,* Vol. 77, (1973), p. 2300.

K.S. Pitzer and G. Mayorga, *J. Solution Chem.,* Vol. 3, (1974), p. 539.

K.S. Pitzer and L.F. Silvester, *J. Solution Chem.,* Vol. 5, (1976), p. 269.

K.S. Pitzer and R.N. Roy, and L.F. Silvester, "Thermodynamics of Electrolytes 7 Sulfuric Acid," *J. Am. Chem. Soc.,* Vol. 99, No. 15, (1977), pp. 4930-4936.

K.S. Pitzer, J.R. Peterson, and L.F. Silvester, "Thermodynamics of Electrolytes. IX. Rare Earth Chlorides, Nitrates, and Perchlorates, "*J. Solution Chem.,* Vol. 7, No. 1, (1978), pp. 45-56.

H. Renon, "Deviation from Ideality in Electrolyte Solutions," *Foundation of Computer-Aided Chemical Process Design, Vol. II, Engineering Foundations,* (1981), New York.

L.F. Silvester and K.S. Pitzer, "Thermodynamics of Electrolytes 8 High-Temperature Properties, Including Enthalpy and Heat Capacity, With Application to Sodium Chloride, "*J. Phys. Chem.,* Vol. 81, No. 19, (1977), pp. 1822-1828.

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