# 2 Thermodynamic Property Models

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

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

## Thermodynamic Property Models

Phases: V = Vapor; L = Liquid; S = Solid. An X indicates applicable to Pure or Mixture.

### Equation-of-State Models

| Property Model | Model Name(s) | Phase(s) | Pure | Mixture |
|---|---|---|---|---|
| ASME Steam Tables | ESH2O0,ESH2O | V L | X | — |
| BWR-Lee-Starling | ESBWR0, ESCSTBWR | V L | X | X |
| Benedict-Webb-Rubin-Starling | ESBWRS, ESBWRS0 | V L | X | X |
| Hayden-O'Connell | ESHOC0,ESHOC | V | X | X |
| HF equation-of-state | ESHF0, ESHF | V | X | X |
| Ideal Gas | ESIG | V | X | X |
| Lee-Kesler | ESLK | V L | — | X |
| Lee-Kesler–Plöcker | ESLKP0,ESLKP | V L | X | X |
| NBS/NRC Steam Tables | ESSTEAM0,ESSTEAM | V L | X | — |
| Nothnagel | ESNTH0,ESNTH | V | X | X |
| Peng-Robinson | ESPR0, ESPR | V L | X | X |
| Standard Peng-Robinson | ESPRSTD0,ESPRSTD | 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 |

| Property Model | Model Name(s) | Phase(s) | Pure | Mixture |
|---|---|---|---|---|
| Redlich-Kwong | ESRK0, ESRK | V | X | X |
| Redlich-Kwong-Aspen | ESRKA0,ESRKA | V L | X | X |
| Standard Redlich-Kwong-Soave | ESRKSTD0,ESRKSTD | V L | X | X |
| Redlich-Kwong-Soave-Boston-Mathias | ESRKS0,ESRKS | V L | X | X |
| Redlich-Kwong-Soave-Wong-Sandler | ESRKSWS0, ESRKSWS | V L | X | X |
| Redlich-Kwong-Soave-MHV2 | ESRKSV20, ESRKSV2 | V L | X | X |
| Schwartzentruber-Renon | ESRKU0,ESRKU | V L | X | X |
| Soave-Redlich-Kwong | ESSRK, ESSRK0 | V L | X | X |
| VPA/IK-CAPE equation-of-state | ESVPA0, ESVPA | V | 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 (Including Electrolyte 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 | L 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 | — |

| Property Model | Model Name | Phase(s) | Pure | Mixture |
|---|---|---|---|---|
| Chao-Seader | PHL0CS | L | X | — |
| Grayson-Streed | PHL0GS | L | X | — |
| Kent-Eisenberg | ESAMIN | L | — | X |
| Maxwell-Bonnell | PL0MXBN | L L1 L2 | X | — |
| Solid Antoine | PS0ANT | S | X | — |

## Heat of Vaporization Models

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

## Molar Volume and Density Models

| Property Model | Model Name | Phase(s) | Pure | Mixture |
|---|---|---|---|---|
| API Liquid Volume | VL2API | L | — | X |
| Brelvi-O'Connell | VL1BROC | L | — | X |
| Clarke Aqueous Electrolyte Volume | VAQCLK | L | — | X |
| Costald Liquid Volume | VL0CTD,VL2CTD | L | X | X |
| Debye-Hückel Volume | VAQDH | L | — | X |
| Liquid Constant Molar Volume | VL0CONS | L | X | — |
| Rackett / DIPPR / IK-CAPE Liquid Volume | VL0RKT,VL2RKT | L | X | — |
| Rackett Mixture Liquid Volume | VL2RKT | L | X | X |
| Modified Rackett | VL2MRK | L | X | X |
| Aspen/DIPPR/IK-CAPE Solid Molar Volume | VS0POLY | S | X | — |
| Liquid Volume Quadratic Mixing Rule | VL2QUAD | L | — | X |

## Heat Capacity Models

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

## Solubility Correlation Models

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

## Other Models

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

# Equation-of-State Models

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

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

| Model | Type |
| --- | --- |
| Redlich-Kwong-Soave-Wong-Sandler | Cubic |
| RK-Soave Alpha functions | Alpha functions |
| Schwartzentruber-Renon | Cubic |
| Soave-Redlich-Kwong | Cubic |
| SRK-Kabadi-Danner | Cubic |
| SRK-ML | Cubic |
| VPA/IK-CAPE equation-of-state | Ideal and association |
| Wong-Sandler mixing rules | Mixing rules |

# ASME Steam Tables

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

## References

*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:

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

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

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

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

| 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 the Aspen Physical Property System for a large number of components. (See *Physical Property Data, Chapter 1*).

## References

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

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

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

# Benedict-Webb-Rubin-Starling

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

The form of the equation-of-state is:

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

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

Where:

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

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

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

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

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

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

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

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

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

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

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

$k_{ij} = k_{ji}$

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

When water is present, by default Benedict-Webb-Rubin-Starling uses the steam table to calculate the enthalpy, entropy, Gibbs energy, and molar volume of water. The total properties are mole-fraction averages of these values with the properties calculated by the equation of state for other

components. Fugacity coefficient is not affected. An option code can disable this use of the steam table.

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

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

## Constants Used with the correlations of Han and Starling

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

| Parameter | Methane | Ethane | Propane | n-Butane |
|---|---|---|---|---|
| $\gamma_i$ | 1.48640 | 2.99656 | 4.56182 | 7.54122 |

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

### References

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

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

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

# Hayden-O'Connell

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

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

Where:

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

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

- For nonpolar, non-associating species:

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

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

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

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

- For polar, associating species:

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

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

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

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

- For chemically bonding species:

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

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

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

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

## Cross-Interactions

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

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

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

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

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

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

$$p = (p_i p_j)^{1/2}$$

$\eta = 0$ 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 the Aspen Physical Property System.

## Chemical Theory

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

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

$$i + j \overset{K_{ij}}{\longleftrightarrow} ij$$
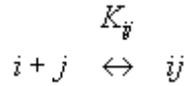
Where *i* and *j* refer to the same component.

The equation-of-state becomes:

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

In this case, molar volume is equal to V/$n^t$.

This represents true total volume over the true number of species $n^t$. However, the reported molar volume is 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. 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 |
| $y_{ii}$ | = | 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 |
|---|---|---|---|---|---|---|

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

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

## References

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

# HF Equation-of-State

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

Species like HF that associate linearly behave as single species. For example, they have a vapor pressure curve, like pure components. The component on which a hypothetical unreacted system is based is often called the apparent (or parent) component. Apparent components react to the true species. Electrolyte Calculation in *Physical Property Methods* 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:

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

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 $1/f$. 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:

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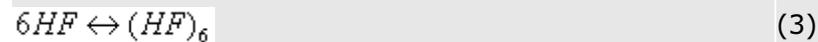
If $p_1$ represents the true partial pressure of the HF monomer, and $p_6$ represents the true partial pressure of the hexamer, then the equilibrium constant is defined as:

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

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 $1/f$ 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 $y = p_1/p$ 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:

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

$$RT \ln K = RT \ln \frac{p_C^v \, p_D^v}{p_A^v \, p_B^v} \tag{14}$$

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:

$$G_m = H_m - T S_m \tag{18}$$

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 Fluoride," *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:

$p = RT / V_m$

# 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,

$$Z^{(0)} = f^{(0)} \left( \frac{T}{T_c}, \frac{P}{P_c} \right)$$

$$Z^{(r)} = f^{(r)} \left( \frac{T}{T_c}, \frac{P}{P_c} \right)$$

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

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

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

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

# Lee-Kesler-Plöcker

The Lee-Kesler-Plöcker equation-of-state is the basis for the LK-PLOCK property method. This equation-of-state applies to hydrocarbon systems that

include the common light gases, such as $H_2S$ and $CO_2$. It can be used in gas-processing, refinery, and petrochemical applications.

The general form of the equation is:

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

Where:

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

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

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

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

The mixing rules are:

| | | |
|---|---|---|
| $V_{cm}$ | $=$ | $\sum_i \sum_j x_i x_j V_{cij}$ |
| $V_{cm}^{1/4} T_c$ | $=$ | $\sum_i \sum_j x_i x_j V_{cij}^{1/4} T_{cij}$ |
| $\omega$ | $=$ | $\sum_i x_i \omega_i$ |
| $Z_m$ | $=$ | $\sum_i x_i Z_{ci}$ |

Where:

| | | |
|---|---|---|
| $V_{cij}$ | $=$ | $\left[ V_{ci}^{1/3} + V_{cj}^{1/3} \right]^3$ |
| $T_{cij}$ | $=$ | $(1 + k_{ij})(T_{ci} T_{cj})^{1/2}$ |
| $Z_{ci}$ | $=$ | $\begin{cases} 0.2905 - 0.085 \omega_i & (\text{Method 1}) \\ p_{ci} V_{ci} / R T_{ci} & (\text{Method 2}) \end{cases}$ |
| $k_{ij}$ | $=$ | $k_{ji}$ |

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

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TCLKP | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| PCLKP | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| VCLKP | $V_{ci}$ | VC | x | 0.001 | 3.5 | MOLE-VOLUME |
| 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($T_{ci}V_{ci}$/ $T_{cj}V_{cj}$) | x | 5.0 | 5.0 | — |

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

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

### References

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

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

# NBS/NRC Steam Tables

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

### References

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

# Nothnagel

The Nothnagel equation-of-state calculates thermodynamic properties for the vapor phase. It is used in property methods NRTL-NTH, UNIQ-NTH, VANL-NTH, and WILS-NTH. It is recommended for systems that exhibit strong vapor phase association. The model incorporates the chemical theory of

dimerization to account for strong association and solvation effects, such as those found in organic acids, like acetic acid. The equation-of-state is:

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

Where:

| | | |
|---|---|---|
| $b$ | = | $\sum_{i=1}^{nc} y_i b_i + \sum_{i=1}^{nc} \sum_{j=1}^{i} y_{ij} b_{ij}$ |
| $b_{ij}$ | = | $(b_i^{1/3} + b_j^{1/3})^3 \Big/ 8$ |
| $nc$ | = | Number of components in the mixture |

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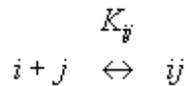
$$i + j \quad \overset{K_{ij}}{\longleftrightarrow} \quad ij$$

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 $V/n^t$ 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: $V/n^a$. Since the apparent number of species is constant and the total volume decreases with association, the quantity $V/n^a$ 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 heat of reaction for the mixed dimerization of components $i$ and $j$ is by default the arithmetic mean of the heats of reaction for the dimerizations of

the individual components. Parameter $\Delta_r H^{\bullet}_{m,ij}$ is a small empirical correction factor to this value:

$$\Delta_r H_{m,ij} = \frac{\Delta_r H_{m,i} + \Delta_r H_{m,j}}{2} + \Delta_r H^{\bullet}_{m,ij}$$

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:

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

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

Parameters you entered:

$$\ln K_{ii} = A_i + B_i\big/_T + C_i \ln T + D_i T$$

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 $K_{ij}$ is computed from

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

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

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

† For the following systems, the values given in Nothnagel et al., 1973 are used by default:

- Methyl chloride/acetone
- Acetonitrile/acetaldehyde
- Acetone/chloroform

- Chloroform/diethyl amine
- Acetone/benzene
- Benzene/chloroform
- Chloroform/diethyl ether
- Chloroform/propyl formate
- Chloroform/ethyl acetate
- Chloroform/methyl acetate
- Chloroform/methyl formate
- Acetone/dichloro methane
- n-Butane/n-perfluorobutane
- n-Pentane/n-perfluoropentane
- n-Pentane/n-perfluorohexane

## 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

The Peng-Robinson equation-of-state is the basis for the PENG-ROB and PR-BM property methods. The model has been implemented with choices of different alpha functions (see Peng-Robinson Alpha Functions) and has been extended to include advanced asymmetric mixing rules.

**Note:** You can choose any of the available alpha functions, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

By default, the PENG-ROB property method uses the literature version of the alpha function and mixing rules. The PR-BM property method uses the Boston-Mathias alpha function and standard mixing rules. These default property methods are recommended for hydrocarbon processing applications such as gas processing, refinery, and petrochemical processes. Their results are comparable to those of the property methods that use the standard Redlich-Kwong-Soave equation-of-state.

When advanced alpha function and asymmetric mixing rules are used with appropriately obtained parameters, the Peng-Robinson model can be used to accurately model polar, non-ideal chemical systems. Similar capability is also available for the Soave-Redlich-Kwong model.

The equation for the Peng-Robinson model is:

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

Where:

| | | |
|---|---|---|
| $b$ | $=$ | $\displaystyle\sum_i x_i b_i$ |
| $c$ | $=$ | $\displaystyle\sum_i x_i c_i$ |
| $a$ | $=$ | $a_0 + a_1$ |
| $a_0$ | $=$ | $\displaystyle\sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{ij})$ (the standard quadratic mixing term, where $k_{ij}$ has been made temperature-dependent) |
| $k_{ij}$ | $=$ | $k_{ij}^{(1)} + k_{ij}^{(2)}T + k_{ij}^{(3)}/T$ $k_{ij} = k_{ji}$ |
| $a_1$ | | $\displaystyle\sum_{i=1}^{n} x_i \left( \sum_{j=1}^{n} x_j ((a_i a_j)^{1/2} l_{i,j})^{1/3} \right)^3$ (an additional, asymmetric term used to model highly non-linear systems) |
| $l_{ij}$ | $=$ | $l_{ij}^{(1)} + l_{ij}^{(2)}T + l_{ij}^{(3)}/T$ In general, $l_{ij} \neq l_{ji}$. |
| $a_i$ | $=$ | $fcn(T, T_{ci}, p_{ci}, \omega_i)$ |
| $b_i$ | $=$ | $fcn(T_{ci}, p_{ci})$ |
| $c_i$ | $=$ | $0.40768 \left( \dfrac{RT_{ci}}{P_{ci}} \right)(0.29441 - z_{RAi})$ |

For best results, the binary parameters $k_{ij}$ and $l_{ij}$ must be determined from regression of phase equilibrium data such as VLE data. The Aspen Physical Property System also has built-in $k_{ij}$ and $l_{ij}$ for a large number of component pairs in the EOS-LIT databank. These parameters are used automatically with the PENG-ROB property method. Values in the databank can be different than those used with other models such as Soave-Redlich-Kwong or Redlich-Kwong-Soave, and this can produce different results.

The model has option codes which can be used to customize the model, by selecting a different alpha function and other model options. See Peng-Robinson Alpha Functions for a description of the alpha functions. See Option Codes for Equation of State Models (under ESPR) for a list of the option codes.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| PRTC | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PRPC | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| OMGPR | $\omega_i$ | OMEGA | x | -0.5 | 2.0 | — |
| PRZRA | $z_{RA}$ | RKTZRA | x | — | — | — |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| PRKBV/1 | $k_{ij}^{(1)}$ | 0 | x | — | — | — |
| PRKBV/2 | $k_{ij}^{(2)}$ | 0 | x | — | — | TEMPERATURE |
| PRKBV/3 | $k_{ij}^{(3)}$ | 0 | x | — | — | TEMPERATURE |
| PRKBV/4 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| PRKBV/5 | $T_{upper}$ | 1000 | x | — | — | TEMPERATURE |
| PRLIJ/1 | $l_{ij}^{(1)}$ | 0 | x | — | — | — |
| PRLIJ/2 | $l_{ij}^{(2)}$ | 0 | x | — | — | TEMPERATURE |
| PRLIJ/3 | $l_{ij}^{(3)}$ | 0 | x | — | — | TEMPERATURE |
| PRLIJ/4 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| PRLIJ/5 | $T_{upper}$ | 1000 | x | — | — | TEMPERATURE |

### 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.

P.M. Mathias, H.C. Klotz, and J.M. Prausnitz, "Equation of state mixing rules for multicomponent mixtures: the problem of invariance," Fluid Phase Equilibria, Vol 67, (1991), pp. 31-44.

# Standard Peng-Robinson

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

**Note:** You can choose any of the available alpha functions, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

The equation for this model is:

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

Where:

| | | |
|---|---|---|
| $b$ | = | $\sum_i x_i b_i$ |
| $a$ | = | $\sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{ij})$ |
| $a_i$ | = | $fcn(T, T_{ci}, p_{ci}, \omega_i)$ |
| $b_i$ | = | $fcn(T_{ci}, p_{ci})$ |

| $k_{ij}$ | $=$ | $k_{ij}^{(1)} + k_{ij}^{(2)}T + k_{ij}^{(3)}/T$ |
| | | $k_{ij} = k_{ji}$ |

The model has option codes which can be used to customize the model, by selecting a different alpha function and other model options. See Peng-Robinson Alpha Functions for a description of the alpha functions. See Option Codes for Equation of State Models (under ESPRSTD) for a list of the option codes.

For best results, the binary parameter $k_{ij}$ must be determined from regression of phase equilibrium data such as VLE data. The Aspen Physical Property System also has built-in $k_{ij}$ for a large number of component pairs in the EOS-LIT databank. These parameters are used automatically with the PENG-ROB property method. Values in the databank can be different than those used with other models such as Soave-Redlich-Kwong or Redlich-Kwong-Soave, and this can produce different results.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TCPRS | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PCPRS | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| OMGPRS | $\omega_i$ | OMEGA | x | -0.5 | 2.0 | — |
| PRKBV/1 | $k_{ij}^{(1)}$ | 0 | x | - | - | - |
| PRKBV/2 | $k_{ij}^{(2)}$ | 0 | x | - | - | TEMPERATURE |
| PRKBV/3 | $k_{ij}^{(3)}$ | 0 | x | - | - | TEMPERATURE |
| PRKBV/4 | $T_{lower}$ | 0 | x | - | - | TEMPERATURE |
| PRKBV/5 | $T_{upper}$ | 1000 | x | - | - | TEMPERATURE |

### References

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


# Peng-Robinson-MHV2

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

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

# Predictive SRK (PSRK)

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

**Note:** You can choose any of the available alpha functions, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

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

# 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.

**Note:** You can choose any of the available alpha functions, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

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

# Redlich-Kwong

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

The equation for the model is:

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

Where:

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

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

$$a_i \quad = \quad 0.42748023 R^2 T_{ci}^{2.5} \Big/ p_{ci}$$

$$b_i \quad = \quad 0.08664035 R T_{ci} \Big/ p_{ci}$$

| 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 |

### 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:

| | | |
|---|---|---|
| $k_{a,ij}$ | = | $k_{a,ij}^0 + k_{a,ij}^1 \dfrac{T}{1000}$ |
| $k_{b,ij}$ | = | $k_{b,ij}^0 + k_{b,ij}^1 \dfrac{T}{1000}$ |

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

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

## 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

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

The equation is:

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

Where:

$$a = a_0 + a_1$$

$a_0$ is the standard quadratic mixing term:

$$a_0 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sqrt{a_i a_j}\,(1 - k_{ij})$$

$a_1$ is an additional, asymmetric (polar) term:

$$a_1 = \sum_{i=1}^{n} x_i \left( \sum_{j=1}^{n} x_j \left( \left( a_i a_j \right)^{1/2} l_{ji} \right)^{1/3} \right)^3$$

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

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

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

$$k_{ij} = k_{ij}^{(1)} + k_{ij}^{(2)} T + k_{ij}^{(3)}/T$$

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

$$l_{ij} = l_{ij}^{(1)} + l_{ij}^{(2)} T + l_{ij}^{(3)}/T \ ; \ \text{in general } l_{ij} \neq l_{ji} \ ; \ l_{jw} = l_{wj} = 0$$

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

**Note:** You can choose any of the available alpha functions, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

The model uses option codes which are described in Soave-Redlich-Kwong Option Codes.

For best results, binary parameters $k_{ij}$ must be determined from phase-equilibrium data regression (for example, VLE data). The Aspen Physical Property System also has built-in $k_{ij}$ for a large number of component pairs in the EOS-LIT databank. These binary parameters are used automatically with the RK-SOAVE property method. Values of $k_{ij}$ in the databank can be different than those used with other models such as Soave-Redlich-Kwong or Standard Peng-Robinson, and this can produce different results.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TCRKSS | $T_{ci}$ | TC | X | 5.0 | 2000.0 | TEMPERATURE |
| PCRKSS | $p_{ci}$ | PC | X | $10^5$ | $10^8$ | PRESSURE |
| OMRKSS | $\omega_i$ | OMEGA | X | -0.5 | 2.0 | — |
| RKSKBV/1 | $k_{ij}^{(1)}$ | 0 | X | -5.0 | 5.0 | — |
| RKSKBV/2 | $k_{ij}^{(2)}$ | 0 | X | — | — | TEMPERATURE |
| RKSKBV/3 | $k_{ij}^{(3)}$ | 0 | X | — | — | TEMPERATURE |
| RKSKBV/4 | $T_{k,lower}$ | 0 | X | — | — | TEMPERATURE |
| RKSKBV/5 | $T_{k,upper}$ | 1000 | X | — | — | TEMPERATURE |
| RKSLBV/1 | $l_{ij}^{(1)}$ | 0 | X | — | — | — |
| RKSLBV/2 | $l_{ij}^{(2)}$ | 0 | X | — | — | TEMPERATURE |
| RKSLBV/3 | $l_{ij}^{(3)}$ | 0 | X | — | — | TEMPERATURE |
| RKSLBV/4 | $T_{l,lower}$ | 0 | X | — | — | TEMPERATURE |
| RKSLBV/5 | $T_{l,upper}$ | 1000 | X | — | — | TEMPERATURE |

### 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.

# Redlich-Kwong-Soave-Boston-Mathias

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

**Note:** You can choose any of the available alpha functions, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

The equation is:

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

Where:

$$a = a_0 + a_1$$

$a_0$ is the standard quadratic mixing term:

$$a_0 = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \sqrt{a_i a_j}\,(1 - k_{ij})$$

$a_1$ is an additional, asymmetric (polar) term:

$$a_1 = \sum_{i=1}^{n} x_i \left( \sum_{j=1}^{n} x_j \left( (a_i a_j)^{1/2} l_{ji} \right)^{1/3} \right)^3$$

$$b = \sum_{i} x_i b_i$$

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

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

$$k_{ij} = k_{ij}^{(1)} + k_{ij}^{(2)}T + k_{ij}^{(3)}/T$$

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

$$l_{ij} = l_{ij}^{(1)} + l_{ij}^{(2)}T + l_{ij}^{(3)}/T \; ; \; \text{in general } l_{ij} \neq l_{ji} \; ; \; l_{jw} = l_{wj} = 0$$

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).

The model uses option codes which are described in Soave-Redlich-Kwong Option Codes.

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

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TCRKS | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PCRKS | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| OMGRKS | $\omega_i$ | OMEGA | x | -0.5 | 2.0 | — |
| RKSKBV/1 | $k_{ij}^{(1)}$ | 0 | x | -5.0 | 5.0 | — |
| RKSKBV/2 | $k_{ij}^{(2)}$ | 0 | x | — | — | TEMPERATURE |
| RKSKBV/3 | $k_{ij}^{(3)}$ | 0 | x | — | — | TEMPERATURE |
| RKSKBV/4 | $T_{k,lower}$ | 0 | x | — | — | TEMPERATURE |
| RKSKBV/5 | $T_{k,upper}$ | 1000 | x | — | — | TEMPERATURE |
| RKSLBV/1 | $l_{ij}^{(1)}$ | 0 | x | — | — | — |
| RKSLBV/2 | $l_{ij}^{(2)}$ | 0 | x | — | — | TEMPERATURE |
| RKSLBV/3 | $l_{ij}^{(3)}$ | 0 | x | — | — | TEMPERATURE |
| RKSLBV/4 | $T_{l,lower}$ | 0 | x | — | — | TEMPERATURE |
| RKSLBV/5 | $T_{l,upper}$ | 1000 | x | — | — | TEMPERATURE |

### References

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

# Redlich-Kwong-Soave-Wong-Sandler

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

**Note:** You can choose any of the available alpha functions, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

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

# Redlich-Kwong-Soave-MHV2

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

**Note:** You can choose any of the available alpha functions, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

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

# Schwartzentruber-Renon

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

The equation for the model is:

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

Where:

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

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

$$c = \sum_i x_i c_i$$

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

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

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

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

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

| | | |
|---|---|---|
| $k_{b,ij}$ | $=$ | $k_{b,ij}^0 + k_{b,ij}^1 T + k_{b,ij}^2 / T$ |
| $k_{a,ii}$ | $=$ | $k_{a,ji}$ |
| $l_{ij}$ | $=$ | $-l_{ji}$ |
| $k_{b,ij}$ | $=$ | $k_{b,ji}$ |

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.

**Warning:** Using $c_{1i}$ and $c_{2i}$ can cause anomalous behavior in enthalpy and heat capacity. Their use is strongly discouraged.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TCRKU | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| PCRKU | $p_{ci}$ | PC | x | 105 | 108 | PRESSURE |
| OMGRKU | $\omega_i$ | 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 ††† | $k_{a,ii}^0$ | 0 | x | — | — | — |
| RKUKA1 ††† | $k_{a,ii}^1$ | 0 | x | — | — | TEMPERATURE |
| RKUKA2 ††† | $k_{a,ii}^2$ | 0 | x | — | — | TEMPERATURE † |
| RKULA0 ††† | $l_{ii}^0$ | 0 | x | — | — | — |
| RKULA1 ††† | $l_{ii}^1$ | 0 | x | — | — | TEMPERATURE |
| RKULA2 ††† | $l_{ii}^2$ | 0 | x | — | — | TEMPERATURE † |
| RKUKB0 ††† | $k_{b,ii}^0$ | 0 | x | — | — | — |
| RKUKB1 ††† | $k_{b,ii}^1$ | 0 | x | — | — | TEMPERATURE |
| RKUKB2 ††† | $k_{b,ii}^2$ | 0 | x | — | — | TEMPERATURE † |

† Absolute temperature units are assumed for $k_{a,ij}^2$, $l_{ij}^2$, and $k_{b,ij}^2$.

†† 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 or Hayden O'Connell models.

## References

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

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

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

# Soave-Redlich-Kwong

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

- A volume translation concept introduced by Peneloux and Rauzy is used to improve molar liquid volume calculated from the cubic equation of state.
- Improvement in water properties is achieved by using the NBS Steam Table.
- Improvement in speed of computation for equation based calculation is achieved by using composition independent fugacity.
- Optional Kabadi-Danner mixing rules for improved phase equilibrium calculations in water-hydrocarbon systems (see SRK-Kabadi-Danner)
- Optional Mathias alpha function

**Note:** You can choose any of the available alpha functions, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

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

The form of the equation-of-state is:

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

Where:

$$a = a_0 + a_1$$

$a_0$ is the standard quadratic mixing term:

$$a_0 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sqrt{a_i a_j} (1 - k_{ij})$$

Where:

$$k_{ij} = k_{ij}^{(1)} + k_{ij}^{(2)} T + k_{ij}^{(3)} / T \; ; \; k_{ij} = k_{ji}$$

$a_1$ is an additional, asymmetric (polar) term:

$$a_1 = \sum_{i=1}^{n} x_i \left( \sum_{j=1}^{n} x_j \left( (a_i a_j)^{1/2} l_{ji} \right)^{1/3} \right)^3$$

Where:

$$l_{ij} = l_{ij}^{(1)} + l_{ij}^{(2)}T + l_{ij}^{(3)}/T \; ; \; \text{in general } l_{ij} \neq l_{ji} \; ; \; l_{jw} = l_{wj} = 0$$

$$b = \sum_i x_i b_i$$

$$c = \sum_i x_i c_i$$

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

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

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

The enthalpy, entropy, Gibbs energy, and molar volume of water are calculated from the steam tables. The total properties are mole-fraction averages of these values with the properties calculated by the equation of state for other components. Fugacity coefficient is not affected.

For best results, the binary parameter $k_{ij}$ must be determined from phase equilibrium data regression (for example, VLE data). The Aspen Physical Property System also has built-in $k_{ij}$ for a large number of component pairs in the SRK-ASPEN databank. These parameters are used automatically with the SRK property method. Values of $k_{ij}$ in the databank can be different than those used with other models such as Standard Redlich-Kwong-Soave or Standard Redlich-Kwong-Soave, and this can produce different results.

The model uses option codes which are described in Soave-Redlich-Kwong Option Codes.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| SRKTC | $T_{ci}$ | TC | X | 5.0 | 2000.0 | TEMPERATURE |
| SRKPC | $p_{ci}$ | PC | X | $10^5$ | $10^8$ | PRESSURE |
| SRKOMG | $\omega_i$ | OMEGA | X | –0.5 | 2.0 | — |
| SRKZRA | $z_{RA}$ | RKTZRA | X | — | — | — |
| SRKKIJ/1 | $k_{ij}^{(1)}$ | 0 | X | — | — | — |
| SRKKIJ/2 | $k_{ij}^{(2)}$ | 0 | X | — | — | TEMPERATURE |
| SRKKIJ/3 | $k_{ij}^{(3)}$ | 0 | X | — | — | TEMPERATURE |
| SRKKIJ/4 | $T_{lower}$ | 0 | X | — | — | TEMPERATURE |
| SRKKIJ/5 | $T_{upper}$ | 1000 | X | — | — | TEMPERATURE |
| SRKLIJ/1 | $l_{ij}^{(1)}$ | 0 | X | — | — | — |
| SRKLIJ/2 | $l_{ij}^{(2)}$ | 0 | X | — | — | TEMPERATURE |
| SRKLIJ/3 | $l_{ij}^{(3)}$ | 0 | X | — | — | TEMPERATURE |
| SRKLIJ/4 | $T_{lower}$ | 0 | X | — | — | TEMPERATURE |
| SRKLIJ/5 | $T_{upper}$ | 1000 | X | — | — | TEMPERATURE |

### References

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

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

P.M. Mathias, H.C. Klotz, and J.M. Prausnitz, "Equation of state mixing rules for multicomponent mixtures: the problem of invariance," Fluid Phase Equilibria, Vol 67, (1991), pp. 31-44.

# SRK-Kabadi-Danner

The SRK-Kabadi-Danner property model uses the SRK equation-of-state with improved phase equilibrium calculations for mixtures containing water and hydrocarbons. These improvements are achieved by using the Kabadi-Danner mixing rules.

The form of the equation-of-state is:

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

Where:

$$a = a_0 + a_{KD}$$

$a_0$ is the standard quadratic mixing term:

$$a_0 = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \sqrt{a_i a_j}(1 - k_{ij})$$

Where:

$$k_{ij} = k_{ij}^{(1)} + k_{ij}^{(2)}T + k_{ij}^{(3)}/T \; ; \; k_{ij} = k_{ji}$$

The best values of $k_{wj}$ ($w$ = water) were obtained from experimental data. Results are given for seven homologous series.

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

| Homologous series | $k_{wi}$ |
|---|---|
| Alkanes | 0.500 |
| Alkenes | 0.393 |
| Dialkenes | 0.311 |
| Acetylenes | 0.348 |
| Naphthenes | 0.445 |
| Cycloalkenes | 0.355 |
| Aromatics | 0.315 |

$a_{KD}$ is the Kabadi-Danner term for water:

$$a_{KD} = \sum_{i=1}^{n} a_{wi}^{"} x_w^2 x_i$$

Where:

$$a_{wi}^{"} = G_i \left[ 1 - \left( \frac{T}{T_{cw}} \right)^{0.80} \right]$$

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

$$G_i = \sum g_l$$

$g_l$ is the group contribution parameter for groups constituting hydrocarbons.

## Groups Constituting Hydrocarbons and Their Group Contribution Parameters

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

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

The model uses option codes which are described in Soave-Redlich-Kwong Option Codes.

SRK-Kabadi-Danner uses the same parameters as SRK, with added interaction parameters. Do not specify values for the SRKLIJ parameters when using SRK-KD.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| SRKTC | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| SRKPC | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| SRKOMG | $\omega_i$ | OMEGA | x | −0.5 | 2.0 | — |
| SRKWF | $G_i$ | 0 | x | — | — | — |

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| SRKZRA | $z_{RA}$ | RKTZRA | x | — | — | — |
| SRKKIJ/1 | $k_{ij}^{(1)}$ | 0 | x | — | — | — |
| SRKKIJ/2 | $k_{ij}^{(2)}$ | 0 | x | — | — | TEMPERATURE |
| SRKKIJ/3 | $k_{ij}^{(3)}$ | 0 | x | — | — | TEMPERATURE |
| SRKKIJ/4 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| SRKKIJ/5 | $T_{upper}$ | 0 | x | — | — | TEMPERATURE |

### References

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

# SRK-ML

The SRK-ML property model is the same as the standard Soave-Redlich-Kwong model with two exceptions:

- $k_{ij}$ may not equal $k_{ji}$; they are unsymmetric, and a different set of parameters are used, as shown below.
- The $l_{ij}$ are calculated from the equation $l_{ij} = k_{ji} - k_{ij}$

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| SRKTCML | $T_{ci}$ | TC | x | 5.0 | 2000.0 | TEMPERATURE |
| SRKPCML | $p_{ci}$ | PC | x | $10^5$ | $10^8$ | PRESSURE |
| SRKOMGML | $\omega_i$ | OMEGA | x | –0.5 | 2.0 | — |
| SRKZRAML | $z_{RA}$ | RKTZRA | x | — | — | — |
| SRKKIJML/1 | $k_{ij}^{(1)}$ | 0 | x | — | — | — |
| SRKKIJML/2 | $k_{ij}^{(2)}$ | 0 | x | — | — | TEMPERATURE |
| SRKKIJML/3 | $k_{ij}^{(3)}$ | 0 | x | — | — | TEMPERATURE |
| SRKKIJML/4 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| SRKKIJML/5 | $T_{upper}$ | 1000 | x | — | — | TEMPERATURE |

# VPA/IK-CAPE Equation-of-State

The VPA/IK-CAPE equation of state is similar to the HF equation of state but allows dimerization, tetramerization and hexamerization to occur simultaneously. The main assumption of the model is that only molecular association causes the gas phase nonideality. Attractive forces between the molecules and the complexes are neglected.

There are three kinds of associations, which can be modeled:

- Dimerization (examples: formic acid, acetic acid)

- Tetramerization (example: acetic acid)
- Hexamerization (example: hydrogen fluoride)

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

## Symbols

In the following description, these symbols are used:

| | | |
|---|---|---|
| $y_i$ | = | Apparent concentration |
| $z_{in}$ | = | True concentration, for component $i$ and degree of association $n=1, 2, 4, 6$ |
| | | $z_{i2} = z_{i4} = z_{i6} = 0 \text{ for } i > 5$ |
| $z_{Mij}$ | = | True concentration of cross-dimers of components $i$ and $j$, for $i,j$ 1 to 5. |
| $p_0$ | = | Reference pressure |
| $k$ | = | Number of components |

## Association Equilibria

Every association equilibrium reaction

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

$$(i) + (j) \leftrightarrow (ij) \tag{2}$$
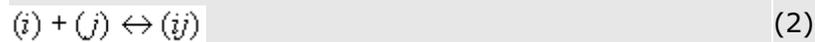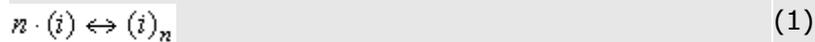
is described by the equilibrium constants

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

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

By setting

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

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

their temperature dependence can be reproduced.

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

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

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

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

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

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

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

Thus, a system of $k$ nonlinear equations for $k$ unknowns $z_{i1}$ has been developed. After having solved it, all the $z_{in}$ and $z_{Mij}$ can be determined using equations (3, 4). This is the main step to evaluate all the properties needed for a calculation.

## Specific Volume of the Gas Phase

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

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

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

The compressibility factor itself is

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

## Fugacity Coefficient

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

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

## Isothermal Enthalpy Departure

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

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

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

with

$$h_i^v = h_i^0 + \int_{T_0}^{T} c_{pi}^{i.g.} dT \tag{13}$$

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

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

and

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

respectively. For the reactions mentioned above:

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

$$(i) + (j) \leftrightarrow (ij) \tag{2}$$
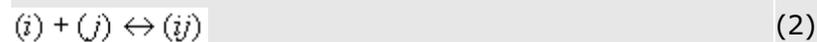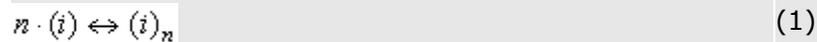
the enthalpies of reaction are

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

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

as the van't Hoff equation

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

holds for this case.

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

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

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

## Isothermal entropy and Gibbs energy departure:

A similar expression for $\Delta g_a$ should hold as it does for the enthalpy departure (eq. 20):

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

using

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

and

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

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

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

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

For $\Delta g_a$ we obtain

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

and, analogously,

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

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

## References

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

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

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# 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.

**Note:** You can choose any of the alpha functions described here, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

This approach was also adopted by Peng and Robinson:

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

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

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \qquad (5)$$

Equations 1 through 5 are the standard Peng-Robinson formulation. The Peng-Robinson alpha function is adequate for hydrocarbons and other nonpolar compounds, but is not sufficiently accurate for polar compounds.

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

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

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

With

| $d_i$ | = | $1 + \dfrac{m_i}{2}$ |
|---|---|---|
| $c_i$ | = | $1 - \dfrac{1}{d_i}$ |

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

## Extended Gibbons-Laughton Alpha Function

The extended Gibbons-Laughton alpha function is suitable for use with both polar and nonpolar components. It has the flexibility to fit the vapor pressure of most substances from the triple point to the critical point.

$$\alpha_i(T) = Max\left(0,\ 1 + X_i(T_{ri} - 1) + Y_i(T_{ri}^{1/2} - 1) + Z_i(T_{ri}^n - 1)\right)$$

Where $T_r$ is the reduced temperature; $X_i$, $Y_i$ and $Z_i$ are substance dependent parameters.

This function is equivalent to the standard Peng-Robinson alpha function if
$$X_i = m_i^2, \; Y = -2m_i(m_i + 1), \text{ and } Z_i = 0.$$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| PRGLP/1 | $X$ | — | X | — | — | — |
| PRGLP/2 | $Y$ | 0 | X | — | — | — |
| PRGLP/3 | $Z$ | 0 | X | — | — | — |
| PRGLP/4 | $n$ | 2 | X | — | — | — |
| PRGLP/5 | $T_{lower}$ | 0 | X | — | — | TEMPERATURE |
| PRGLP/6 | $T_{upper}$ | 1000 | X | — | — | TEMPERATURE |

## Twu Generalized Alpha Function

The Twu generalized alpha function is a theoretically-based function that is currently recognized as the best available alpha function. It behaves better than other functions at supercritical conditions ($T > T_c$) and when the acentric factor is large. The improved behavior at high values of acentric factor is important for high molecular weight pseudocomponents. There is no limit on the minimum value of acentric factor that can be used with this function.

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

$$\alpha^{(0)} = T_r^{N^{(0)}(M^{(0)}-1)} \exp\left[L^{(0)}(1 - T_r^{N^{(0)}M^{(0)}})\right]$$

$$\alpha^{(1)} = T_r^{N^{(1)}(M^{(1)}-1)} \exp\left[L^{(1)}(1 - T_r^{N^{(1)}M^{(1)}})\right]$$

Where the $L$, $M$, and $N$ are parameters that vary depending on the equation of state and whether the temperature is above or below the critical temperature of the component.

For Peng-Robinson equation of state:

|  | Subcritical T | Supercritical T |
|---|---|---|
| $L^{(0)}$ | 0.272838 | 0.373949 |
| $M^{(0)}$ | 0.924779 | 4.73020 |
| $N^{(0)}$ | 1.19764 | -0.200000 |
| $L^{(1)}$ | 0.625701 | 0.0239035 |
| $M^{(1)}$ | 0.792014 | 1.24615 |
| $N^{(1)}$ | 2.46022 | -8.000000 |

## Twu Alpha Function

The Twu alpha function is a theoretically-based function that is currently recognized as the best available alpha function. It behaves better than other functions at supercritical conditions ($T > T_c$).

$$\alpha = T_r^{N(M-1)} \exp\left[L(1 - T_r^{NM})\right]$$

Where the L, M, and N are substance-dependent parameters that must be determined from regression of pure-component vapor pressure data or other data such as liquid heat capacity.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| PRTWUP/1 | L | — | X | — | — | — |
| PRTWUP/2 | M | 0 | X | — | — | — |
| PRTWUP/3 | N | 0 | X | — | — | — |

## Mathias-Copeman Alpha Function

This is an extension of the Peng-Robinson alpha function which provides a more accurate fit of vapor pressure for polar compounds.

$$\alpha_i(T) = [1 + c_{1,i}(1 - T_{ri}^{1/2}) + c_{2,i}(1 - T_{ri}^{1/2})^2 + c_{3,i}(1 - T_{ri}^{1/2})^3]^2 \quad (7)$$

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

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

## Schwartzentruber-Renon-Watanasiri Alpha Function

The Schwartzentruber-Renon-Watanasiri alpha function is:

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

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

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

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

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

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| OMGPR | $\omega_i$ | OMEGA | X | -0.5 | 2.0 | — |
| PRSRP/1 | $p_{1i}$ | — | X | — | — | — |
| PRSRP/2 | $p_{2,i}$ | 0 | X | — | — | — |
| PRSRP/3 | $p_{3i}$ | 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 Methods | Model** form.

| Alpha function | Model name | First Option code |
|---|---|---|
| Standard Peng Robinson | ESPRSTD0, ESPRSTD | 1 |
| Standard PR/ Boston-Mathias | ESPR0, ESPR<br>ESPRWS0, ESPRWS<br>ESPRV20, ESPRV2 | 0<br>0<br>0 |
| Extended Gibbons-Laughton | ESPR0, ESPR | 2 |
| Twu Generalized alpha function | ESPR0, ESPR | 3 |
| Twu alpha function | ESPR0, ESPR | 4 |
| 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.

C.H. Twu, J. E. Coon, and J.R. Cunningham, "A New Cubic Equation of State," Fluid Phase Equilib., Vol. 75, (1992), pp. 65-79.

C.H. Twu, D. Bluck, J.R. Cunningham, and J.E. Coon, "A Cubic Equation of State with a New Alpha Function and a New Mixing Rule," Fluid Phase Equilib., Vol. 69, (1991), pp. 33-50.

# Soave Alpha Functions

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

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

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

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

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

**Note:** You can choose any of the alpha functions described here, but you cannot define multiple property methods based on this model using different alpha functions within the same run.

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

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

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

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

## Soave Modification

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

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

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

$$m_i = 0.48508 + 1.55171 \omega_i - 0.15613 \omega_i^2 \tag{6}$$

Equations 1, 2, 3, 5 and 6 are the standard Redlich-Kwong-Soave formulation. The Soave alpha function is adequate for hydrocarbons and other nonpolar compounds, but is not sufficiently accurate for polar compounds.

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

## Boston-Mathias Extrapolation

For light gases at high reduced temperatures (> 5), equation 5 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:

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

With

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

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

Where:

| $m_i$ | = | Computed by equation 6 |
|---|---|---|
| Equation 5 | = | Used for subcritical temperatures |

Additional parameters are not needed.

## Mathias Alpha Function

This is an extension of the Soave alpha function which provides a more accurate fit of vapor pressure for polar compounds.

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

For $\eta_i$=0, equation 8 reduces to the standard Redlich-Kwong-Soave formulation, equations 5 and 6. For temperatures above critical, the Boston-Mathias extrapolation is used, that is, equation 7 with:

$$d_i = 1 + \frac{m_i}{2} + 0.3\eta_i \qquad (9)$$

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

The Mathias alpha function is used in the Redlich-Kwong-Aspen model, which is the basis for the RK-ASPEN property method. This alpha function is also available as an option for SRK, SRKKD, SRK-ML, RK-SOAVE, and RKS-BM. See Soave-Redlich-Kwong Option Codes for more information.

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

† RKAPOL for Redlich-Kwong-Aspen, SRKPOL for SRK and SRKKD, SRKMLP for SRK-ML, RKSPOL for RKS-BM, or RKSSPO for RK-SOAVE.

## Extended Mathias Alpha Function

An extension of the Mathias approach is:

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

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

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

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

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

This alpha function is used in the Redlich-Kwong-UNIFAC model which is the basis for the SR-POLAR property method.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TCRKU | $T_{ci}$ | TC | X | 5.0 | 2000.0 | TEMPERATURE |
| PCRKU | $p_{ci}$ | PC | X | $10^5$ | $10^8$ | PRESSURE |
| OMGRKU | $\omega_i$ | 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 is suitable for use with both polar and nonpolar components. It has the flexibility to fit the vapor pressure of most substances from the triple point to the critical point.

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

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

pressure data to regress the constants. If the temperature is supercritical, set $c_{2,i}$ and $c_{3,i}$ to 0.

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

## Schwartzentruber-Renon-Watanasiri Alpha Function

The Schwartzentruber-Renon-Watanasiri alpha function is:

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

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. 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 7 with:

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

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

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

## Extended Gibbons-Laughton Alpha Function

The extended Gibbons-Laughton alpha function is suitable for use with both polar and nonpolar components. It has the flexibility to fit the vapor pressure of most substances from the triple point to the critical point.

$$\alpha_i(T) = Max\left(0, \; 1 + X_i(T_{ri} - 1) + Y_i(T_{ri}^{1/2} - 1) + Z_i(T_{ri}^n - 1)\right)$$

Where $T_r$ is the reduced temperature; $X_i$, $Y_i$ and $Z_i$ are substance dependent parameters.

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This function is equivalent to the standard Soave alpha function if

$$X_i = m_i^2, \ Y = -2m_i\left(m_i + 1\right), \text{ and } Z_i = 0.$$

This function is not intended for use in supercritical conditions. To avoid predicting negative alpha, when $T_{ri} > 1$ the Boston-Mathias alpha function is used instead.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| RKSGLP/1 | $X$ | — | X | — | — | — |
| RKSGLP/2 | $Y$ | 0 | X | — | — | — |
| RKSGLP/3 | $Z$ | 0 | X | — | — | — |
| RKSGLP/4 | $n$ | 2 | X | — | — | — |
| RKSGLP/5 | $T_{lower}$ | 0 | X | — | — | TEMPERATURE |
| RKSGLP/6 | $T_{upper}$ | 1000 | X | — | — | TEMPERATURE |

## Twu Generalized Alpha Function

The Twu generalized alpha function is a theoretically-based function that is currently recognized as the best available alpha function. It behaves better than other functions at supercritical conditions ($T > T_c$) and when the acentric factor is large. The improved behavior at high values of acentric factor is important for high molecular weight pseudocomponents. There is no limit on the minimum value of acentric factor that can be used with this function.

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

$$\alpha^{(0)} = T_r^{N^{(0)}(M^{(0)}-1)} \exp\left[L^{(0)}(1 - T_r^{N^{(0)}M^{(0)}})\right]$$

$$\alpha^{(1)} = T_r^{N^{(1)}(M^{(1)}-1)} \exp\left[L^{(1)}(1 - T_r^{N^{(1)}M^{(1)}})\right]$$

Where the $L$, $M$, and $N$ are parameters that vary depending on the equation of state and whether the temperature is above or below the critical temperature of the component.

For Soave-Redlich-Kwong:

| | Subcritical T | Supercritical T |
|---|---|---|
| $L^{(0)}$ | 0.544000 | 0.379919 |
| $M^{(0)}$ | 1.01309 | 5.67342 |
| $N^{(0)}$ | 0.935995 | -0.200000 |
| $L^{(1)}$ | 0.544306 | 0.0319134 |
| $M^{(1)}$ | 0.802404 | 1.28756 |
| $N^{(1)}$ | 3.10835 | -8.000000 |

## 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 Methods | Models** sheet.

| Alpha Function | Model Name | First Option Code |
|---|---|---|

| Alpha Function | Model Name | First Option Code |
|---|---|---|
| original RK | ESRK0, ESRK | — |
| standard RKS | ESRKSTD0, ESRKSTD | — |
| standard RKS/Boston-Mathias | ESRKS0, ESRKS<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) |
| Twu generalized | ESRKSTD0, ESRKSTD, ESRKS, ESRKS0, ESSRK, ESSRK0, ESRKSML, ESRKSML0 | 5 |
| Gibbons-Laughton with Patel extension | ESRKSTD0, ESRKSTD, ESRKS, ESRKS0, ESSRK, ESSRK0, ESRKSML, ESRKSML0 | 3 |
| Mathias for T < Tc; Boston-Mathias for T > Tc | ESRKSTD0, ESRKSTD, ESRKS, ESRKS0, ESSRK, ESSRK0, ESRKSML, ESRKSML0 | 4 |

## 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.

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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.

C.H. Twu, W.D. Sim, and V. Tassone, "Getting a Handle on Advanced Cubic Equations of State", Chemical Engineering Progress, Vol. 98 #11 (November 2002) pp. 58-65.

# 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:

$$G_m^E = RT \ln \varphi - \sum_i x_i RT \ln \varphi_i^* \qquad (1)$$

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:

$$V(p = \infty) = b \qquad (2)$$

$$V^E(p = \infty) = 0 \qquad (3)$$

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 Physical Property System equation-of-state models:

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

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

### 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:

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

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 $\alpha$:

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

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) 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)). 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).

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

# Predictive Soave-Redlich-Kwong-Gmehling Mixing Rules

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

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

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

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

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

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

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

With:

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

Therefore:

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

The mixing rule is:

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

Where $\Lambda'$ 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). 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:

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

(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 the Aspen Physical Property System are activated when using the PSRK equation-of-state model.

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

## References

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

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

# 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).

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.) 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):

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

The excess Helmholtz energy is almost independent of pressure. It can be approximated by the Gibbs energy at low pressure. The difference between the two functions is corrected by fitting $k_{ij}$ until the excess Gibbs energy from the equation-of-state (using the mixing rules 3 and 8) is equal to the excess Gibbs energy computed by an activity coeffecient model. This is done at a specific mole fraction and temperature.

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

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

## References

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

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

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

# Activity Coefficient Models

The Aspen Physical Property System has the following 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 |
| Cosmo-SAC | Regular solution |
| Electrolyte NRTL | Electrolyte |
| Ideal Liquid | Ideal |
| NRTL (Non-Random-Two-Liquid) | Local composition |

| Model | Type |
|---|---|
| Pitzer | Electrolyte |
| Polynomial Activity Coefficient | Arithmetic |
| Redlich-Kister | Arithmetic |
| Scatchard-Hildebrand | Regular solution |
| Three-Suffix Margules | Arithmetic |
| UNIFAC | Group contribution |
| UNIFAC (Lyngby modified) | Group contribution |
| UNIFAC (Dortmund modified) | Group contribution |
| UNIQUAC | Local composition |
| Van Laar | Regular solution |
| Wagner interaction parameter | Arithmetic |
| Wilson | Local composition |
| Wilson with Liquid Molar Volume | Local composition |

# Bromley-Pitzer Activity Coefficient Model

The Bromley-Pitzer activity coefficient model is a simplified Pitzer activity coefficient model with Bromley correlations for the interaction parameters. See Working Equations for a detailed description. This model has predictive capabilities. It can be used to compute activity coefficients for aqueous electrolytes up to 6 molal ionic strength, but is less accurate than the Pitzer model if the parameter correlations are used. The model should not be used for mixed-solvent electrolyte systems.

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

Parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$, and $\theta$ 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 | 0 | — |

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

# Working Equations

The complete Pitzer equation (Fürst and Renon, 1982) for the excess Gibbs energy is (see also equation 4):

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

Where:

| | | |
|---|---|---|
| $G^E$ | = | Excess Gibbs energy |
| $R$ | = | Gas constant |
| $T$ | = | Temperature |
| $n_w$ | = | Kilograms of water |
| $z_i$ | = | Charge number of ion $i$ |
| $m_i = \dfrac{x_i}{x_w} \left( \dfrac{M_w}{1000} \right) = \dfrac{n_i}{n_w}$ | = | molality of ion $i$ |

Where:

| | | |
|---|---|---|
| $x_i$ | = | Mole fraction of ion $i$ |
| $x_w$ | = | Mole fraction of water |
| $M_w$ | = | Molecular weight of water (g/mol) |
| $n_i$ | = | Moles of ion $i$ |

$B$, $C$, $\theta$ and $\Psi$ are interaction parameters, and $f(I)$ is an electrostatic term as a function of ionic strength; these terms are discussed in Pitzer Activity Coefficient Model, which has 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.

$$\frac{G^E}{RT} = n_W \left[ f(I) + \sum_i \sum_j B_{ij} m_i m_j + \sum_i \sum_j \theta_{ij} m_i m_j \right]$$ (2)

Where:

$$B_{ij} \quad = \quad f(\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}, \beta_{ij}^{(3)})$$

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.

### References

L.A. Bromley, "Thermodynamic Properties of Strong Electrolytes in Aqueous Solution, " *AIChE J.*, Vol. 19, No. 2, (1973), pp. 313 – 320.

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.

## Parameter Conversion

For *n-m* electrolytes, *n* and *m*>1 (2-2, 2-3, 3-4, and so on), the parameter $\beta^{(3)}$ corresponds to Pitzer's $\beta^{(1)}$; $\beta^{(2)}$ is the same in both Aspen Physical Property System and original Pitzer models. Pitzer refers to the *n-m* electrolyte parameters as $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(0)}$. $\beta^{(0)}$ and $\beta^{(2)}$ retain their meanings in both models, but Pitzer's $\beta^{(1)}$ is Aspen Physical Property System $\beta^{(3)}$. Be careful to make this distinction when entering *n-m* electrolyte parameters.

## Chien-Null

The Chien-Null model calculates liquid activity coefficients and it can be used for highly non-ideal systems. The generalized expression used in its derivation

can be adapted to represent other well known formalisms for the activity coefficient by properly defining its binary terms. This characteristic allows the model the use of already available binary parameters regressed for those other liquid activity models with thermodynamic consistency.

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

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

Where:

$R_{ji} = A_{ji} / A_{ij}$

$A_{ii} = 0$

$A_{ij} \neq A_{ji}$

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

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).

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

Where:

| | | |
|---|---|---|
| $V_i^{*,l}$ | = | 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 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:)

$V_{ji} = S_{ji} = A_{ji} / A_{ij}$

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).

$S_{ji} = R_{ji}A_{ji} / A_{ij}$

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

$V_{ji} = G_{ji}$

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

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

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

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

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

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

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 | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|
| ICHNUL | — | 3 | 1 | 6 | — |
| CHNULL/1 | $a_{ij}$ | 0 | — | — | — |
| CHNULL/2 | $b_{ij}$ | 0 | — | — | — |
| CHNULL/3 | $V_{ij}$ | 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 |
|---|---|---|---|---|---|---|

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

# COSMO-SAC

Cosmo-SAC is a solvation model that describes the electric fields on the molecular surface of species that are polarizable. It requires a fairly complicated quantum mechanical calculation, but this calculation must be done only once for a particular molecule; then the results can be stored. In its final form, it uses individual atoms as the building blocks for predicting phase equilibria instead of functional groups. This model formulation provides a considerably larger range of applicability than group-contribution methods.

The calculation for liquid nonideality is only slightly more computationally intensive than activity-coefficient models such as NRTL or UNIQUAC. Cosmo-SAC complements the UNIFAC group-contribution method, because it is applicable to virtually any mixture.

The Cosmo-SAC model calculates liquid activity coefficients. The equation for the Cosmo-SAC model is:

$$\ln \gamma_i = \frac{A_i}{a_{eff}} \sum_{\sigma_m} p_i(\sigma_m) \left[ \ln \Gamma_S(\sigma_m) - \ln \Gamma_i(\sigma_m) \right] + \ln \gamma_i^{SG}$$

With

$$\ln \Gamma_S(\sigma_m) = -\ln \left\{ \sum_{\sigma_n} p_S(\sigma_n) \Gamma_S(\sigma_n) \exp \left[ \frac{-\Delta W(\sigma_m, \sigma_n)}{kT} \right] \right\}$$

$$\ln \Gamma_i(\sigma_m) = -\ln \left\{ \sum_{\sigma_n} p_i(\sigma_n) \Gamma_i(\sigma_n) \exp \left[ \frac{-\Delta W(\sigma_m, \sigma_n)}{kT} \right] \right\}$$

$$p_i(\sigma) = \frac{A_i(\sigma)}{A_i}$$

$$p_S(\sigma) = \frac{\sum_i x_i A_i p_i(\sigma)}{\sum_i x_i A_i}$$

$$A_i = \sum_{\sigma} A_i(\sigma)$$

$$\Delta W(\sigma_m, \sigma_n) = \frac{\alpha'}{2} (\sigma_m + \sigma_n)^2 + \Delta W^{HB}(\sigma_m, \sigma_n)$$

$$\ln \gamma_i^{SG} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j}$$

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

$$r_i = \frac{V_i}{V_{eff}}$$

$$q_i = \frac{A_i}{A_{eff}}$$

Where:

| | |
|---|---|
| $\gamma_i$ | = Activity coefficient of component $i$ |
| $\gamma_i^{SG}$ | = Staverman-Guggenheim model for combinatorial contribution to $\gamma_i$ |
| $\Gamma_i(\sigma_m)$ | = Segment activity coefficient of segment $\sigma_m$ in component $i$ |
| $\Gamma_S(\sigma_m)$ | = Segment activity coefficient of segment $\sigma_m$ in solvent mixture |
| $p_i(\sigma_m)$ | = Sigma profile of component $i$ |
| $p_i(\sigma_m)$ | = Sigma profile of solvent mixture |
| $\sigma$ | = Surface charge density |
| $\Delta W(\sigma_m, \sigma_n)$ | = Exchange energy between segments $\sigma_m$ and $\sigma_n$ |
| $\Delta W^{HB}(\sigma_m, \sigma_n)$ | = Hydrogen-bonding contribution to exchange energy between segments $\sigma_m$ and $\sigma_n$ |
| $z$ | = Coordination number, 10 |
| $V_i$ | = Molecular volume of component $i$ |
| $A_i$ | = Molecular surface area of component $i$ |
| $a_{eff}$ | = Standard segment surface area, 7.50 Å$^2$ |
| $V_{eff}$ | = Standard component volume, 66.69 Å$^3$ |
| $A_{eff}$ | = Standard component surface area, 79.53 Å$^2$ |
| $\alpha'$ | = Misfit energy constant |

The Cosmo-SAC model does not require binary parameters. For each component, it has six input parameters. **CSACVL** is the component volume parameter which is always defined in cubic angstroms, regardless of chosen

units sets. **SGPRF1** to **SGPRF5** are five component sigma profile parameters; each can store up to 12 points of sigma profile values. All six input parameters are obtained from COSMO calculation. The Aspen Physical Property System includes a database of sigma profiles for over 1400 compounds from Mullins et al. (2006). The parameters were obtained by permission from the Virginia Tech Sigma Profile Database website (http://www.design.che.vt.edu/VT-2004.htm). Aspen Technology, Inc. does not claim proprietary rights to these parameters.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CSACVL | $V_i$ | — | x | — | — | VOLUME ($Å^3$) |
| SGPRF1 | $A_i p_i(1\text{-}12)$ | — | x | — | — | — |
| SGPRF2 | $A_i p_i(13\text{-}24)$ | — | x | — | — | — |
| SGPRF3 | $A_i p_i(25\text{-}36)$ | — | x | — | — | — |
| SGPRF4 | $A_i p_i(37\text{-}48)$ | — | x | — | — | — |
| SGPRF5 | $A_i p_i(49\text{-}51)$ | — | x | — | — | — |

## Option Codes

The primary version of COSMO-SAC is the model by Lin and Sandler (2002). Two other versions are available using an option code, as detailed in the table below:

| Option Code | Description |
|---|---|
| 1 | COSMO-SAC model by Lin and Sandler (2002) |
| 2 | COSMO-RS model by Klamt and Eckert (2000) |
| 3 | Lin and Sandler model with modified exchange energy (Lin et al., 2002) |

## References

A. Klamt and F. Eckert, "COSMO-RS: A Novel and Efficient Method for the a Priori Prediction of Thermophysical Data of Liquids," *Fluid Phase Equilibria* 43, 172 (2000).

S.-T. Lin, P. M. Mathias, Y. Song, C.-C. Chen, and S. I. Sandler, "Improvements of Phase-Equilibrium Predictions for Hydrogen-Bonding Systems from a New Expression for COSMO Solvation Models," presented at the AIChE Annual Meeting, Indianapolis, IN, 3-8 November (2002).

S.-T. Lin and S. I. Sandler, "A Priori Phase Equilibrium Prediction from a Segment Contribution Solvation Model," *Ind. Eng. Chem. Res.* 41, 899 (2002).

E. Mullins, et al. "Sigma-Profile Database for Using COSMO-Based Thermodynamic Methods," *Ind. Eng. Chem. Res.* 45, 4389 (2006).

# 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 NRTL 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.

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

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 *Physical Property Data*, Chapter 1).

Certain Electrolyte NRTL activity coefficient model parameters are used with reciprocal temperature terms:

- CPDIEC
- NRTL/2
- GMELCD for electrolyte-electrolyte or electrolyte-molecule pairs

When any of these parameters is specified, absolute temperature units are used for the calculations in this model.

Option codes can affect the performance of this model. See Option Codes for Activity Coefficient Models for details.

| Parameter Name | Symbol | No. of Elements | Default | MDS | Units |
|---|---|---|---|---|---|
| **Dielectric Constant Unary Parameters** | | | | | |
| CPDIEC | $A_B$ | 1 | — | — | — |
| | $B_B$ | 1 | 0 | — | — |
| | $C_B$ | 1 | 298.15 | — | TEMPERATURE[†] |
| **Ionic Born Radius Unary Parameters** | | | | | |
| RADIUS | $r_i$ | 1 | $3\times10^{-10}$ | — | 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[†] |

| Parameter Name | Symbol | No. of Elements | Default | MDS | Units |
|---|---|---|---|---|---|
| **Dielectric Constant Unary Parameters** | | | | | |
| | $D_{B,ca}$ | 1 | 0 | x | TEMPERATURE[†] |
| GMELCE | $E_{ca,B}$ | 1 | 0 | x | — |
| | $E_{B,ca}$ | 1 | 0 | x | — |
| GMELCN | $\alpha_{ca,B} = \alpha_{B,ca}$ | 1 | .2 | x | — |
| **Electrolyte-Electrolyte Pair Parameters** | | | | | |
| GMELCC | $C_{ca',ca''}$ | 1 | 0 | x | — |
| | $C_{ca'',ca'}$ | 1 | 0 | x | — |
| | $C_{c'a,c''a}$ | 1 | 0 | x | — |
| | $C_{c''a,c'a}$ | 1 | 0 | x | — |
| GMELCD | $D_{ca',ca''}$ | 1 | 0 | x | TEMPERATURE [†] |
| | $D_{ca'',ca'}$ | 1 | 0 | x | TEMPERATURE[†] |
| | $D_{c'a,c''a}$ | 1 | 0 | x | TEMPERATURE[†] |
| | $D_{c''a,c'a}$ | 1 | 0 | x | TEMPERATURE[†] |
| GMELCE | $E_{ca',ca''}$ | 1 | 0 | x | — |
| | $E_{ca'',ca'}$ | 1 | 0 | x | — |
| | $E_{c'a,c''a}$ | 1 | 0 | x | — |
| | $E_{c''a,c'a}$ | 1 | 0 | x | — |
| GMELCN | $\alpha_{ca',ca''} = \alpha_{ca'',ca'}$ | 1 | .2 | x | — |
| | $\alpha_{c'a,c''a} = \alpha_{c''a,c'a}$ | 1 | .2 | x | — |

[†] Certain Electrolyte NRTL activity coefficient model parameters are used with reciprocal temperature terms:

- CPDIEC
- NRTL/2
- GMELCD for electrolyte-electrolyte or electrolyte-molecule pairs

When any of these parameters is specified, absolute temperature units are used for the calculations in this model.

Reference: 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.

# Theoretical Basis and Working Equations

In this section, 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-Debye-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-Debye-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 of *Physical Property Methods*.

## References

C.-C. Chen, H.I. Britt, J.F. Boston, and L.B. Evans, "Local Compositions Model for Excess Gibbs Energy of Electrolyte Systems: Part I: Single Solvent, Single

Completely Dissociated Electrolyte Systems:, *AIChE J.*, Vol. 28, No. 4, (1982), p. 588-596.

C.-C. Chen, and L.B. Evans, "A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems," *AIChE J.*, Vol. 32, No. 3, (1986), p. 444-459.

B. Mock, L.B. Evans, and C.-C. Chen, "Phase Equilibria in Multiple-Solvent Electrolyte Systems: A New Thermodynamic Model," Proceedings of the 1984 Summer Computer Simulation Conference, p. 558.

B. Mock, L.B. Evans, and C.-C. Chen, "Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems," *AIChE J.*, Vol. 32, No. 10, (1986), p. 1655-1664.

## Long-Range Interaction Contribution

The Pitzer-Debye-Hückel formula, normalized to mole fractions of unity for solvent and zero for electrolytes, is used to represent the long-range interaction contribution.

$$\frac{G_m^{*E,PDH}}{RT} = -\left(\sum_k x_k\right)\left(\frac{1000}{M_B}\right)^{\frac{1}{2}}\left(\frac{4A_\varphi I_x}{\rho}\right)\ln\left(1+\rho I_x^{\frac{1}{2}}\right) \tag{3}$$

Where:

| | | |
|---|---|---|
| $x_k$ | = | Mole fraction of component $k$ |
| $M_B$ | = | Molecular weight of the solvent B |
| $A_\varphi$ | = | Debye-Hückel parameter: |
| $A_\varphi$ | = | $\frac{1}{3}\left(\frac{2\pi N_A d}{1000}\right)^{\frac{1}{2}}\left(\frac{Q_e^2}{\varepsilon_w kT}\right)^{\frac{3}{2}}$ (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): |
| $I_x$ | = | $\frac{1}{2}\sum_i x_i z_i^2$ (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.

$$\ln \gamma_i^{*PDH} = -\left(\frac{1000}{M_B}\right)^{1/2} A_\varphi \left[\left(\frac{2z_i^2}{\rho}\right) \ln\left(1+\rho I_x^{1/2}\right) + \frac{z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1+\rho I_x^{1/2}}\right]$$

(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.

$$\frac{G_m^{*E,Born}}{RT} = \frac{Q_e^2}{2kT}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_w}\right)\left(\frac{\sum_i x_i z_i^2}{r_i}\right)10^{-2}$$

(7)

Where:

| | | |
|---|---|---|
| $r_i$ | = | Born radius |

The expression for the activity coefficient can be derived from (7):

$$\ln \gamma_i^{*Born} = \frac{Q_e^2}{2kT}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_w}\right)\frac{z_i^2}{r_i}10^{-2}$$

(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:

$$\frac{X_{ji}}{X_{ii}} = \left(\frac{X_j}{X_i}\right)G_{ji}$$

(9)

Where:

| | | |
|---|---|---|
| $X_j$ | = | $x_j C_j$ |
| | | ($C_j = z_j$ for ions and $C_j$ = unity for molecules) |
| $G_{ji}$ | = | $e^{\left(-\alpha_{ji}\tau_{ji}\right)}$ |
| $\tau_{ji}$ | = | $\dfrac{g_{ji} - g_{ii}}{RT}$ |
| $\alpha_{ji}$ | = | 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 ($g_{ij} = g_{ji}$ and $\alpha_{ij} = \alpha_{ji}$).

Similarly,

$$\frac{X_{ji}}{X_{ki}} = \left(\frac{X_j}{X_k}\right) G_{ji,ki} \tag{10}$$

Where:

| | | |
|---|---|---|
| $G_{ji,ki}$ | = | $e^{\left(-\alpha_{ji,ki}\tau_{ji,ki}\right)}$ |
| $\tau_{ji,ki}$ | = | $\dfrac{g_{ji} - g_{ki}}{RT}$ |
| $\alpha_{ji,ki}$ | = | Nonrandomness factor |

## Apparent Binary Systems

The derivations that follow are based on a simple system of one completely dissociated liquid electrolyte *ca* and one solvent *B*. They will be later extended to multicomponent systems. In this simple system, three different arrangements exist:



solvent at
center

cation at
center

anion at
center
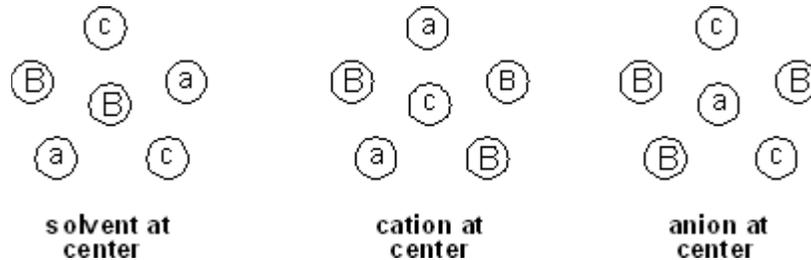
In the case of a central solvent molecule with other solvent molecules, cations, and anions in its immediate neighborhood, the principle of local electroneutrality is followed: the surrounding cations and anions are such that the neighborhood of the solvent is electrically neutral. In the case of a central cation (anion) with solvent molecules and anions (cations) in its immediate neighborhood, the principle of like-ion repulsion is followed: no ions of like charge exist anywhere near each other, whereas opposite charged ions are very close to each other.

The effective local mole fractions are related by the following expressions:

$$X_{cB} + X_{aB} + X_{BB} = 1 \text{ (central solvent cells)} \tag{11}$$

$$X_{Bc} + X_{ac} = 1 \text{ (central cation cells)} \tag{12}$$

$$X_{Ba} + X_{ca} = 1 \text{ (central anion cells)} \tag{13}$$

Using equation 11 through 13 and the notation introduced in equations 9 and 10 above, expressions for the effective local mole fractions in terms of the overall mole fractions can be derived.

$$X_{iB} = \frac{X_i G_{iB}}{X_a G_{cB} + X_c G_{cB} + X_B G_{BB}} \qquad i = c, a, \text{ or } B \qquad (14)$$

$$X_{ac} = \frac{X_a}{X_a + X_B G_{Bc,ac}} \qquad (15)$$

$$X_{ca} = \frac{X_c}{X_c + X_B G_{Bn,ca}} \qquad (16)$$

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:

$$G_m(c-cell) = z_c(X_{Bc} g_{Bc} + X_{ac} g_{ac}) \qquad (17)$$

$$G_m(a-cell) = z_a(X_{Bn} g_{Ba} + X_{ca} g_{ca}) \qquad (18)$$

$$G_m(B-cell) = X_{aB} g_{aB} + X_{cB} g_{cB} + X_{BB} g_{BB} \qquad (19)$$

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:

$$G_m(c-cell) = z_c g_{ac} \qquad (20)$$

$$G_m(a-cell) = z_a g_{ca} \qquad (21)$$

$$G_m(B-cell) = g_{BB} \qquad (22)$$

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:

$$G_m^{E,lc} = x_m\left(G_m(B-cell) - G_m^{ref}(B-cell)\right) + x_c\left(G_m(c-cell) - G_m^{ref}(c-cell)\right) \qquad (23)$$
$$+ x_a\left(G_m(a-cell) - G_m^{ref}(a-cell)\right)$$

Using the previous relation for the excess Gibbs energy and the expressions for the residual and reference Gibbs energy (equations 17 to 19 and 20 to 22), the following expression for the excess Gibbs energy is obtained:

$$\frac{G_m^{E,lc}}{RT} = X_B X_{cB} \tau_{cB} + X_B X_{aB} \tau_{aB} + X_c X_{Bc} z_c \tau_{Bc,ac} + X_a X_{Bn} z_a \tau_{Bn,ca} \qquad (24)$$

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.

$$\frac{1}{z_c} \ln \gamma_c^{*lc} = \frac{X_B^2 \tau_{cB} G_{cB}}{\left( X_c G_{cB} + X_a G_{aB} + X_B \right)^2} + \frac{X_a \tau_{Ba} X_B G_{Ba}}{\left( X_c + X_B G_{Ba} \right)^2}$$
$$+ \frac{X_B \tau_{Bc} G_{Bc}}{\left( X_a + X_B G_{Bc} \right)} - \tau_{Bc} - G_{cB} \tau_{cB} \tag{34}$$

$$\frac{1}{z_a}\ln\gamma_a^{*k} = \frac{X_B^2\tau_{aB}G_{aB}}{\left(X_cG_{cB}+X_aG_{aB}+X_B\right)^2} + \frac{X_c\tau_{Bc}X_BG_{Bc}}{\left(X_a+X_BG_{Bc}\right)^2}$$

$$+ \frac{X_B\tau_{Ba}G_{Ba}}{\left(X_c+X_BG_{Ba}\right)} - \tau_{Ba} - G_{aB}\tau_{aB}$$

(35)

$$\ln\gamma_B^k = X_{cB}\tau_{cB} + X_{aB}\tau_{aB} + \frac{X_cG_{Bc}\tau_BX_a}{\left(X_a+G_{Bc}X_B\right)^2} + \frac{X_aG_{Ba}\tau_{Ba}X_c}{\left(X_c+G_{Ba}X_B\right)^2}$$

$$- \frac{X_cX_BG_{cB}\tau_{cB}}{\left(X_cG_{cB}+X_aG_{aB}+X_B\right)^2} - \frac{X_aX_BG_{aB}\tau_{aB}}{\left(X_cG_{cB}+X_aG_{aB}+X_B\right)^2}$$

(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:

$$\ln\gamma_B^k = \frac{\sum_j X_j G_{jB}\tau_{jB}}{\sum_k X_k G_{kB}} + \sum_B \frac{X_B G_{BB}}{\sum_k X_k G_{kB}}\left(\tau_{BB} - \frac{\sum_k X_k G_{kB'}\tau_{kB}}{\sum_k X_k G_{kB'}}\right)$$

$$+ \sum_c\sum_{a'}\frac{X_a}{\sum_{a'}X_{a''}}\frac{X_c G_{Bc,a'c}}{\sum_k X_k G_{kc,a'c}}\left(\tau_{Bc,a'c} - \frac{\sum_k X_k G_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}}\right)$$

$$+ \sum_a\sum_c\frac{X_c}{\sum_{c''}X_{c''}}\frac{X_a G_{Ba,c'a}}{\sum_k X_k G_{ka,c'a}}\left(\tau_{Bc,c'a} - \frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}}\right)$$

(38)

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:

$$\frac{1}{z_a}\ln\gamma_a^{lc} = \sum_{c'}\left(\frac{X_{c'}}{\sum_{c''}X_{c''}}\right)\frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} + \sum_B \frac{X_{Bm} G_{aB}}{\sum_k X_k G_{kB}}\left(\tau_{aB} - \frac{\sum_k X_k G_{kB}\tau_{kB}}{\sum_k X_k G_{kB}}\right)$$
$$+ \sum_c\sum_{a'}\left(\frac{X_{a'}}{\sum_{a''}X_{a''}}\right)\frac{X_c G_{ac,a'c}}{\sum_k X_k G_{kc,a'c}}\left(\tau_{ac,a'c} - \frac{\sum_k X_k G_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}}\right)$$
(40)

Where:

$$G_{cB} = \frac{\sum_a X_a G_{ca,B}}{\sum_{a'}X_{a'}}$$
(41)

$$G_{aB} = \frac{\sum_c X_c G_{ca,B}}{\sum_{c'}X_{c'}}$$
(42)

$$\alpha_{Bc} = \alpha_{cB} = \frac{\sum_a X_a \alpha_{B,ca}}{\sum_{a'}X_{a'}}$$
(43)

$$\alpha_{Ba} = \alpha_{aB} = \frac{\sum_c X_c \alpha_{B,ca}}{\sum_{c'}X_{c'}}$$
(44)

$$\tau_{cB} = -\frac{\ln G_{cB}}{\alpha_{cB}}$$
(45)

$$\tau_{aB} = -\frac{\ln G_{aB}}{\alpha_{cB}}$$
(46)

$$\tau_{Ba,ca} = \tau_{aB} - \tau_{ca,B} + \tau_{B,ca}$$
(47)

$$\tau_{Bc,ac} = \tau_{cB} - \tau_{ca,B} + \tau_{B,ca}$$
(48)

# Parameters

The model adjustable parameters include:

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

Note that for the electrolyte-electrolyte pair parameters, the two electrolytes must share either one common cation or one common anion.

Each type of the electrolyte NRTL parameter consists of both the nonrandomness factor, $\alpha$, 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 Debye-Hückel limiting law. Calculation results with electrolyte-molecule and electrolyte-electrolyte pair parameters fixed to zero should be adequate for very dilute weak electrolyte systems; however, for concentrated systems, pair parameters are required for accurate representation.

See *Physical Property Data*, Chapter 1, for the pair parameters available from the electrolyte NRTL model databank. The table contains pair parameters for some electrolytes in aqueous solution at 100°C. These values were obtained

by using the Aspen Physical Property Data Regression System (DRS) to regress vapor pressure and mole fraction data at T=100°C with SYSOP15S (*Handbook of Chemistry and Physics*, 56th Edition, CRC Press, 1975, p. E-1). 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.

# ENRTL-SAC

eNRTL-SAC (**ENRTLSAC**, patent pending) is an extension of the nonrandom two-liquid segment activity coefficient model (NRTL-SAC, patent pending) by Chen and Song (Ind. Eng. Chem. Res., 2004, 43, 8354) to include electrolytes in the solution. It can be used in usable in Aspen Properties and Aspen Polymers Plus. It is intended for the computation of ionic activity coefficients and solubilities of electrolytes, organic and inorganic, in common solvents and solvent mixtures. In addition to the three types of molecular parameters defined for organic nonelectrolytes in NRTL-SAC (hydrophobicity *X*, hydrophilicity *Z*, and polarity *Y-* and *Y+*)*,* an electrolyte parameter, *E*, is introduced to characterize both local and long-range ion-ion and ion-molecule interactions attributed to ionized segments of electrolytes.

In applying the segment contribution concept to electrolytes, a new conceptual electrolyte segment *e* corresponding to the electrolyte parameter *E*, is introduced. This conceptual segment *e* would completely dissociate to a cationic segment (*c*) and an anionic segment (*a*), both of unity charge. All electrolytes, organic or inorganic, symmetric or unsymmetric, univalent or multivalent, are to be represented with this conceptual uni-univalent electrolyte segment *e* together with previously defined hydrophobic segment *x*, polar segments *y-* and *y+*, and hydrophilic segment *z* in NRTL-SAC.

A major consideration in the extension of NRTL-SAC for electrolytes is the treatment of the reference state for activity coefficient calculations. While the conventional reference state for nonelectrolyte systems is the pure liquid component, the conventional reference state for electrolytes in solution is the infinite-dilution aqueous solution and the corresponding activity coefficient is *unsymmetric*. The equation for the logarithm of the unsymmetric activity coefficient of an ionic species is

$$\ln \gamma_I^* = \ln \gamma_I^{*lc} + \ln \gamma_I^{*PDH} + \ln \gamma_I^{*FH} + \Delta \ln \gamma_I^{Born}$$

With

$$\ln \gamma_I^{*lc} = \ln \gamma_I^{lc} - \ln \gamma_I^{\infty lc} = \sum_i r_{i,I} \left[ \ln \Gamma_i^{lc} - \ln \Gamma_i^{\infty lc} \right]$$

$$\ln \gamma_I^{*PDH} = \sum_m r_{m,I} \ln \Gamma_m^{*PDH} + r_{c,I} \ln \Gamma_c^{*PDH} + r_{a,I} \ln \Gamma_a^{*PDH}$$

$$\ln \gamma_I^{*FH} = \ln \gamma_I^{FH} - \ln \gamma_I^{\infty FH} = r_I - \ln \left( \sum_J x_J r_J \right) - \frac{r_I}{\sum_J x_J r_J}$$

$$\Delta \ln \gamma_I^{Born} = r_{c,I} \Delta \ln \Gamma_c^{Born} + r_{a,I} \Delta \ln \Gamma_a^{Born}$$

$$\ln \Gamma_m^{lc} = \frac{\sum_j x_j G_{jm} \tau_{jm}}{\sum_k x_k G_{km}} + \sum_{m'} \frac{x_{m'} G_{mm'}}{\sum_k x_k G_{km'}} \left( \tau_{mm'} - \frac{\sum_j x_j G_{jm'} \tau_{jm'}}{\sum_k x_k G_{km'}} \right)$$

$$+ \frac{x_c G_{mc,ac}}{\sum_k x_k G_{kc,ac}} \left( \tau_{mc,ac} - \frac{\sum_j x_j G_{jc,ac} \tau_{jc,ac}}{\sum_k x_k G_{kc,ac}} \right)$$

$$+ \frac{x_a G_{ma,ca}}{\sum_k x_k G_{ka,ca}} \left( \tau_{ma,ca} - \frac{\sum_j x_j G_{ja,ca} \tau_{ja,ca}}{\sum_k x_k G_{ka,ca}} \right)$$

$$\ln \Gamma_c^{lc} = \sum_m \frac{x_m G_{cm}}{\sum_k x_k G_{km}} \left( \tau_{cm} - \frac{\sum_j x_j G_{jm} \tau_{jm}}{\sum_k x_k G_{km}} \right) + \frac{\sum_j x_j G_{jc,ac} \tau_{jc,ac}}{\sum_k x_k G_{kc,ac}}$$

$$- \frac{x_a}{\sum_k x_k G_{ka,ca}} \left( \frac{\sum_j x_j G_{ja,ca} \tau_{ja,ca}}{\sum_k x_k G_{ka,ca}} \right)$$

$$\ln \Gamma_a^{lc} = \sum_m \frac{x_m G_{am}}{\sum_k x_k G_{km}} \left( \tau_{am} - \frac{\sum_j x_j G_{jm} \tau_{jm}}{\sum_k x_k G_{km}} \right) + \frac{\sum_j x_j G_{ja,ca} \tau_{ja,ca}}{\sum_k x_k G_{ka,ca}}$$

$$- \frac{x_c}{\sum_k x_k G_{kc,ac}} \left( \frac{\sum_m x_m G_{mc,ac} \tau_{mc,ac}}{\sum_k x_k G_{kc,ac}} \right)$$

$$\ln \Gamma_i^{\infty lc} = \ln \Gamma_i^{lc} (x_W = 1)$$

$$r_I = \sum_m r_{I,m} + r_{I,c} + r_{I,a}$$

$$x_j = \frac{\sum_I x_I r_{I,j}}{\sum_I \sum_i x_I r_{I,i}}$$

$$\tau_{cm} = \tau_{cm} = \tau_{cm}$$

$$\tau_{mc,ac} = \tau_{ma,ca} = \tau_{mc}$$

$$G = \exp(-\alpha \tau)$$

$$\ln \Gamma_m^{*PDH} = 2 \left( \frac{1000}{\bar{M}_s} \right)^{\frac{1}{2}} \frac{A_\varphi I_x^{\frac{3}{2}}}{1 + \rho I_x^{\frac{1}{2}}}$$

$$\ln \Gamma_c^{*PDH} = \ln \Gamma_a^{*PDH} = -\left( \frac{1000}{\bar{M}_s} \right)^{\frac{1}{2}} A_\varphi \left[ \left( \frac{2}{\rho} \right) \ln \left( 1 + \rho I_x^{\frac{1}{2}} \right) + \frac{I_x^{\frac{1}{2}} - 2 I_x^{\frac{3}{2}}}{1 + \rho I_x^{\frac{1}{2}}} \right]$$

$$A_\varphi = \frac{1}{3} \left( \frac{2\pi N_A \bar{d}_s}{1000} \right)^{\frac{1}{2}} \left( \frac{Q_e^2}{\bar{\varepsilon}_s k_B T} \right)^{\frac{3}{2}}$$

$$I_x = \frac{1}{2} (x_c + x_a)$$

$$\bar{M}_s = \sum_S x_S' M_S$$

$$\frac{1}{\bar{d}_s} = \sum_S \frac{x_S'}{d_S}$$

$$\bar{\varepsilon}_s = \sum_S w_S' \varepsilon_S$$

$$x_S' = \frac{x_S}{\sum_S x_S}$$

$$w_S' = \frac{M_S x_S}{\sum_S M_S x_S}$$

$$\Delta \ln \Gamma_c^{Born} = \frac{Q_e^2}{2 k_B T} \left( \frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w} \right) \frac{1}{r_c} 10^{-2}$$

$$\Delta \ln \Gamma_a^{Born} = \frac{Q_e^2}{2 k_B T} \left( \frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w} \right) \frac{1}{r_a} 10^{-2}$$

Where:

| | | |
|---|---|---|
| $I, J$ | = | Component index |
| $i, j, m, c, a$ | = | Conceptual segment index |
| $m$ | = | Conceptual molecular segment, $x$, $y-$, $y+$, $z$ |
| $c$ | = | Conceptual cationic segment |
| $a$ | = | Conceptual anionic segment |
| $i, j$ | = | $m,c,a$ |
| $\gamma_I^*$ | = | Unsymmetric activity coefficient of an ionic species $I$ |
| $\gamma_I^{*lc}$ | = | NRTL term |

| | | |
|---|---|---|
| $\gamma_I^{*PDH}$ | = | Pitzer-Debye-Hückel term |
| $\gamma_I^{*FH}$ | = | Flory-Huggins term |
| $\infty$ | = | Aqueous-phase infinite-dilution reference state |
| $\Gamma_i$ | = | Activity coefficient of conceptual segment $i$ |
| $r_I$ | = | Total segment number of component $I$ |
| $x_I$ | = | Mole fraction of component $I$ |
| $r_{I,i}$ | = | Number of conceptual segment $i$ containing in component $I$ |
| $x_i$ | = | Segment mole fraction of conceptual segment $i$ in mixtures |
| $\alpha_{ij}$ | = | NRTL binary non-randomness factor parameter for conceptual segments |
| $\tau_{ij}$ | = | NRTL binary interaction energy parameter for conceptual segments |
| $A_\varphi$ | = | Debye-Hückel parameter |
| $\rho$ | = | Closest approach parameter, 14.9 |
| $I_x$ | = | Ionic strength (segment mole fraction scale) |
| $\bar{M}_s$ | = | Average solvent molecular weight, g/mol |
| $\bar{d}_s$ | = | Average solvent density, g/cm$^3$ |
| $N_A$ | = | Avogadro's number |
| $Q_e$ | = | Absolute electronic charge |
| $\bar{\varepsilon}_s$ | = | Average solvent dielectric constant |
| $\varepsilon_w$ | = | Water dielectric constant |
| $r_c$ | = | Born radius of cationic segment |
| $r_a$ | = | Born radius of anionic segment |

## NRTL binary parameters for conceptual segments

The NRTL binary parameters between conceptual molecular segments in are determined by available VLE and LLE data between reference molecules defined in NRTLSAC.

| Segment (1) | x | x | y- | y+ | x |
|---|---|---|---|---|---|
| Segment (2) | y- | z | z | z | y+ |
| $\tau_{12}$ | 1.643 | 6.547 | -2.000 | 2.000 | 1.643 |
| $\tau_{21}$ | 1.834 | 10.949 | 1.787 | 1.787 | 1.834 |
| $\alpha_{12} = \alpha_{21}$ | 0.2 | 0.2 | 0.3 | 0.3 | 0.2 |

NaCl is used as the reference electrolyte for the conceptual electrolyte segment $e$. The NRTL binary parameters between conceptual molecular

segments and the electrolyte segment $e$ are determined from literature data or preset as follows:

| Segment (1) | x | y- | y+ | z |
|---|---|---|---|---|
| Segment (2) | e | e | e | e |
| $\tau_{12}$ | 15 | 12 | 12 | 8.885 |
| $\tau_{21}$ | 5 | -3 | -3 | -4.549 |
| $\alpha_{12} = \alpha_{21}$ | 0.2 | 0.2 | 0.2 | 0.2 |

## Parameters used in ENRTLSAC

Each component can have up to five parameters, $r_{I,i}$ ($i$ = x, y-, y+, z, e), although only one or two of these parameters are needed for most solvents and ionic species in practice. Since conceptual segments apply to all species, these five parameters are implemented together as a binary parameter, **NRTLXY(*I, i*)** where **_I_** represents a component index and **_i_** represents a conceptual segment index.

## Option codes

There are three option codes in **ENRTLSAC**. The first is used to enable or disable the Flory-Huggins term. The other two are only used internally and you should not change their values. The Flory-Huggins term is included by default in eNRTL-SAC model. You can remove this term using the first option code. The table below lists the values for the first option code.

| 0 | Flory-Huggins term included (default) |
|---|---|
| Others | Flory-Huggins term removed |

## References

C.-C. Chen and Y. Song, "Solubility Modeling with a Nonrandom Two-Liquid Segment Activity Coefficient Model," Ind. Eng. Chem. Res. 43, 8354 (2004).

C.-C. Chen and Y. Song, "Extension of Nonrandom Two-Liquid Segment Activity Coefficient Model for Electrolytes," Ind. Eng. Chem. Res. 44, 8909 (2005).

# Hansen

Hansen is a solubility parameter model and is commonly used in the solvent selection process. It is based on the regular solution theory and Hansen solubility parameters. This model has no binary parameters and its application merely follows the empirical guide *like dissolves like*.

The Hansen model calculates liquid activity coefficients. The equation for the Hansen model is:

$$\ln \gamma_i = \frac{V_i}{RT}\left[(\delta_i^d - \bar{\delta}^d)^2 + 0.25(\delta_i^p - \bar{\delta}^p)^2 + 0.25(\delta_i^h - \bar{\delta}^h)^2\right] + \ln\frac{V_i}{\bar{V}} + 1 - \frac{V_i}{\bar{V}}$$

with

$$\bar{\delta}^d = \sum_i \phi_i \delta_i^d$$

$$\bar{\delta}^p = \sum_i \phi_i \delta_i^p$$

$$\bar{\delta}^h = \sum_i \phi_i \delta_i^h$$

$$\phi_i = \frac{x_i V_i}{\bar{V}}$$

$$\bar{V} = \sum_i x_i V_i$$

Where:

| | | |
|---|---|---|
| $\gamma_i$ | = | Activity coefficient of component $i$ |
| $V_i$ | = | Molar volume of component $i$ |
| $\delta_i^d$ | = | Hansen solubility parameter of component $i$ for nonpolar effect |
| $\delta_i^p$ | = | Hansen solubility parameter of component $i$ for polar effect |
| $\delta_i^h$ | = | Hansen solubility parameter of component $i$ for hydrogen-bonding effect |
| $\phi_i$ | = | Volume fraction of component $i$ |
| $x_i$ | = | Mole fraction of component $i$ |
| $R$ | = | Gas constant |
| $T$ | = | Temperature |

The Hansen model does not require binary parameters. For each component, it has four input parameters.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| DELTAD | $\delta_i^d$ | — | x | — | — | PRESSURE^0.5 |
| DELTAP | $\delta_i^p$ | — | x | — | — | PRESSURE^0.5 |
| DELTAH | $\delta_i^h$ | — | x | — | — | PRESSURE^0.5 |
| HANVOL | $V_i$ | — | x | — | — | VOLUME |

## Option codes

The Hansen volume is implemented as an input parameter. If the Hansen volume is not input by the user it will be calculated by an Aspen Plus internal method. You can also request the Aspen Plus method using Option Codes in Aspen Plus Interface. The table below lists the option codes.

## First Option Code in Hansen model

| 0 | Hansen volume input by user (default) |
|---|---|
| Other values | Hansen volume calculated by Aspen Plus |

### Reference

Frank, T. C.; Downey, J. R.; Gupta, S. K. "Quickly Screen Solvents for Organic Solids," *Chemical Engineering Progress* 1999, *December*, 41.

Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press, 2000.

# 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:

| $G_{ij}$ | = | $\exp\left(-\alpha_{ij}\tau_{ij}\right)$ |
|---|---|---|
| $\tau_{ij}$ | = | $a_{ij} + \dfrac{b_{ij}}{T} + e_{ij}\ln T + f_{ij}T$ |
| $\alpha_{ij}$ | = | $c_{ij} + d_{ij}(T - 273.15K)$ |
| $\tau_{ii}$ | = | 0 |
| $G_{ii}$ | = | 1 |

$a_{ij}$, $b_{ij}$, $c_{ij}$, and $f_{ij}$ are unsymmetrical. That is, $a_{ij}$ may not be equal to $a_{ji}$, etc.

## Recommended $c_{ij}$ Values for Different Types of Mixtures

| $c_{ij}$ | Mixtures |
|---|---|
| 0.30 | Nonpolar substances; nonpolar with polar non-associated liquids; small deviations from ideality |
| 0.20 | Saturated hydrocarbons with polar non-associated liquids and systems that exhibit liquid-liquid immiscibility |
| 0.47 | Strongly self-associated substances with nonpolar substances |

The binary parameters $a_{ij}$, $b_{ij}$, $c_{ij}$, $d_{ij}$, $e_{ij}$, and $f_{ij}$ can be determined from VLE and/or LLE data regression. The Aspen Physical Property System has a large number of built-in binary parameters for the NRTL model. The binary parameters have been regressed using VLE and LLE data from the Dortmund Databank. The binary parameters for the VLE applications were regressed using the ideal gas, Redlich-Kwong, and Hayden O'Connell equations of state. See *Physical Property Data*, Chapter 1, for details.

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

The NRTL-2 property method uses data set 2 for NRTL. All other NRTL methods use data set 1.

## 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.

# NRTL-SAC

NRTL-SAC (patent pending) is a segment contribution activity coefficient model, derived from the Polymer NRTL model, usable in Aspen Properties and Aspen Polymers Plus. NRTL-SAC can be used for fast, qualitative estimation of the solubility of complex organic compounds in common solvents. Conceptually, the model treats the liquid non-ideality of mixtures containing complex organic molecules (solute) and small molecules (solvent) in terms of interactions between three pairwise interacting conceptual segments: hydrophobic segment ($x$), hydrophilic segment ($z$), and polar segments ($y-$ and $y+$). In practice, these conceptual segments become the molecular descriptors used to represent the molecular surface characteristics of each solute or solvent molecule. Hexane, water, and acetonitrile are selected as the reference molecules for the hydrophobic, hydrophilic, and polar segments, respectively. The molecular parameters for all other solvents can be determined by regression of available VLE or LLE data for binary systems of solvent and the reference molecules or their substitutes. The treatment results in four component-specific molecular parameters: hydrophobicity $X$,

hydrophilicity *Z*, and polarity *Y*- and *Y*+. The two types of polar segments, *Y*- and *Y*+, are used to reflect the wide variations of interactions between polar molecules and water.

The conceptual segment contribution approach in NRTL-SAC represents a practical alternative to the UNIFAC functional group contribution approach. This approach is suitable for use in the industrial practice of carrying out measurements for a few selected solvents and then using NRTL-SAC to quickly predict other solvents or solvent mixtures and to generate a list of suitable solvent systems.

The NRTL-SAC model calculates liquid activity coefficients. The equation for the NRTL-SAC model is:

$$\ln \gamma_I = \ln \gamma_I^C + \ln \gamma_I^R$$

with

$$\ln \gamma_I^C = \ln \gamma_I^{FH} = \ln \frac{\phi_I}{x_I} + 1 - p_I \sum_J \frac{\phi_J}{p_J}$$

$$\ln \gamma_I^R = \ln \gamma_I^{lc} = \sum_m r_{m,I} \left[ \ln \Gamma_m^{lc} - \ln \Gamma_m^{lc,I} \right]$$

$$\ln \Gamma_m^{lc} = \frac{\sum_i x_i G_{im} \tau_{im}}{\sum_i x_i G_{im}} + \sum_i \frac{x_i G_{mi}}{\sum_j x_j G_{ji}} \left( \tau_{mi} - \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_j x_j G_{ji}} \right)$$

$$\ln \Gamma_m^{lc,I} = \frac{\sum_i x_{I,i} G_{im} \tau_{im}}{\sum_i x_{I,i} G_{im}} + \sum_i \frac{x_{I,i} G_{mi}}{\sum_j x_{I,j} G_{ji}} \left( \tau_{mi} - \frac{\sum_j x_{I,j} G_{ji} \tau_{ji}}{\sum_j x_{I,j} G_{ji}} \right)$$

$$\phi_I = \frac{p_I x_I}{\sum_I p_I x_I}$$

$$p_I = s_I (r_I)^{\tau_I}$$

$$r_I = \sum_m r_{I,m}$$

$$x_i = \frac{\sum_I x_I r_{I,i}}{\sum_I \sum_i x_I r_{I,i}}$$

$$x_{I,i} = \frac{r_{I,i}}{\sum_i r_{I,i}}$$

$G = \exp(-\alpha\tau)$

Where:

| | | |
|---|---|---|
| $I, J$ | = | Component index |
| $i, j, m$ | = | Conceptual segment index $x$, $y$-, $y$+, $z$ |
| $\gamma_I$ | = | Activity coefficient of component $I$ |
| $\gamma_I^C = \gamma_I^{FH}$ | = | Flory-Huggins term for combinatorial contribution to $\gamma_I$ |
| $\gamma_I^R = \gamma_I^{lc}$ | = | NRTL term for local composition interaction contribution to $\gamma_I$ |
| $\phi_I$ | = | Segment mole fraction of component $I$ |
| $p_I$ | = | Effective component size parameter |
| $s_I$ and $\varepsilon_I$ | = | Empirical parameters for $p_I$ |
| $r_I$ | = | Total segment number of component $I$ |
| $x_I$ | = | Mole fraction of component $I$ |
| $r_{I,m}$ | = | Number of conceptual segment $m$ containing in component $I$ |
| $x_i$ | = | Segment mole fraction of conceptual segment $i$ in mixtures |
| $\alpha_{im}$ | = | NRTL binary non-randomness factor parameter for conceptual segments |
| $\tau_{im}$ | = | NRTL binary interaction energy parameter for conceptual segments |

## NRTL binary parameters for conceptual segments

The NRTL binary parameters between conceptual segments in NRTL-SAC are determined by available VLE and LLE data between reference molecules defined above.

| Segment 1 | $x$ | $x$ | $y$- | $y$+ | $x$ |
|---|---|---|---|---|---|
| Segment 2 | $y$- | $z$ | $z$ | $z$ | $y$+ |
| $\tau_{12}$ | 1.643 | 6.547 | -2.000 | 2.000 | 1.643 |
| $\tau_{21}$ | 1.834 | 10.949 | 1.787 | 1.787 | 1.834 |
| $\alpha_{12} = \alpha_{21}$ | 0.2 | 0.2 | 0.3 | 0.3 | 0.2 |

## Parameters used in NRTL–SAC

Each component can have up to four parameters, $r_{I,x}$, $r_{I,y\text{-}}$, $r_{I,y+}$, and $r_{I,z}$ although only one or two of these molecular parameters are needed for most solvents in practice. Since conceptual segments apply to all molecules, these four molecular parameters are implemented together as a binary parameter, **NRTLXY(_I, m_)** where **_I_** represents a component (molecule) index and **_m_** represents a conceptual segment index.

In addition, the Flory-Huggins size parameter, FHSIZE , is used in NRTL-SAC to calculate the effective component size parameter, $p_I$. The Flory-Huggins combinatorial term can be turned off by setting $\varepsilon_I = 0$ for each component in mixtures.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units | Comment |
|---|---|---|---|---|---|---|---|
| NRTLXY | $r_{I,m}$ | — | — | — | — | — | Binary, symmetric |
| FHSIZE/1 | $s_I$ | 1.0 | — | 1E-15 | 1E15 | — | Unary |
| FHSIZE/2 | $\varepsilon_I$ | 1.0 | — | -1E10 | 1E10 | — | Unary |

## Option codes

The Flory-Huggins term is included by default in the NRTL-SAC model. You can remove this term using the first option code. The table below lists the values for this option code.

| 0 | Flory-Huggins term included (default) |
|---|---|
| Others | Flory-Huggins term removed |

## NRTL-SAC molecular parameters for common solvents

The molecular parameters are identified for 62 solvents and published.

| Solvent name | $r_{I,x}$ | $r_{I,y-}$ | $r_{I,y+}$ | $r_{I,z}$ |
|---|---|---|---|---|
| ACETIC-ACID | 0.045 | 0.164 | 0.157 | 0.217 |
| ACETONE | 0.131 | 0.109 | 0.513 | |
| ACETONITRILE | 0.018 | 0.131 | 0.883 | |
| ANISOLE | 0.722 | | | |
| BENZENE | 0.607 | | 0.190 | |
| 1-BUTANOL | 0.414 | 0.007 | | 0.485 |
| 2-BUTANOL | 0.335 | 0.082 | | 0.355 |
| N-BUTYL-ACETATE | 0.317 | 0.030 | 0.330 | |
| METHYL-TERT-BUTYL-ETHER | 1.040 | 0.219 | 0.172 | |
| CARBON-TETRACHLORIDE | 0.718 | | 0.141 | |
| CHLOROBENZENE | 0.710 | | 0.424 | |
| CHLOROFORM | 0.278 | | 0.039 | |
| CUMENE | 1.208 | | 0.541 | |
| CYCLOHEXANE | 0.892 | | | |
| 1,2-DICHLOROETHANE | 0.394 | | 0.691 | |
| 1,1-DICHLOROETHYLENE | 0.529 | | 0.208 | |
| 1,2-DICHLOROETHYLENE | 0.188 | | 0.832 | |
| DICHLOROMETHANE | 0.321 | | 1.262 | |
| 1,2-DIMETHOXYETHANE | 0.081 | 0.194 | 0.858 | |
| N,N-DIMETHYLACETAMIDE | 0.067 | 0.030 | 0.157 | |

| Solvent name | $r_{I,x}$ | $r_{I,v-}$ | $r_{I,v+}$ | $r_{I,z}$ |
|---|---|---|---|---|
| N,N-DIMETHYLFORMAMIDE | 0.073 | 0.564 | 0.372 | |
| DIMETHYL-SULFOXIDE | 0.532 | 2.890 | | |
| 1,4-DIOXANE | 0.154 | 0.086 | 0.401 | |
| ETHANOL | 0.256 | 0.081 | | 0.507 |
| 2-ETHOXYETHANOL | 0.071 | 0.318 | | 0.237 |
| ETHYL-ACETATE | 0.322 | 0.049 | 0.421 | |
| ETHYLENE-GLYCOL | | 0.141 | | 0.338 |
| DIETHYL-ETHER | 0.448 | 0.041 | 0.165 | |
| ETHYL-FORMATE | 0.257 | | 0.280 | |
| FORMAMIDE | | 0.089 | 0.341 | 0.252 |
| FORMIC-ACID | 0.707 | 2.470 | | |
| N-HEPTANE | 1.340 | | | |
| N-HEXANE | 1.000 | | | |
| ISOBUTYL-ACETATE | 1.660 | | 0.108 | |
| ISOPROPYL-ACETATE | 0.552 | 0.154 | 0.498 | |
| METHANOL | 0.088 | 0.149 | 0.027 | 0.562 |
| 2-METHOXYETHANOL | 0.052 | 0.043 | 0.251 | 0.560 |
| METHYL-ACETATE | 0.236 | | 0.337 | |
| 3-METHYL-1-BUTANOL | 0.419 | | 0.538 | 0.314 |
| METHYL-BUTYL-KETONE | 0.673 | 0.224 | 0.469 | |
| METHYLCYCLOHEXANE | 1.162 | | 0.251 | |
| METHYL-ETHYL-KETONE | 0.247 | 0.036 | 0.480 | |
| METHYL-ISOBUTYL-KETONE | 0.673 | 0.224 | 0.469 | |
| ISOBUTANOL | 0.566 | | 0.067 | 0.485 |
| N-METHYL-2-PYRROLIDONE | 0.197 | 0.322 | | 0.305 |
| NITROMETHANE | 0.025 | | 1.216 | |
| N-PENTANE | 0.898 | | | |
| 1-PENTANOL | 0.474 | 0.223 | 0.426 | 0.248 |
| 1-PROPANOL | 0.375 | 0.030 | | 0.511 |
| ISOPROPYL-ALCOHOL | 0.351 | 0.070 | 0.003 | 0.353 |
| N-PROPYL-ACETATE | 0.514 | 0.134 | 0.587 | |
| PYRIDINE | 0.205 | 0.135 | 0.174 | |
| SULFOLANE | 0.210 | | | 0.457 |
| TETRAHYDROFURAN | 0.235 | 0.040 | 0.320 | |

| Solvent name | $r_{I,x}$ | $r_{I,y-}$ | $r_{I,y+}$ | $r_{I,z}$ |
|---|---|---|---|---|
| 1,2,3,4-TETRAHYDRONAPHTHALENE | 0.443 | 0.555 | | |
| TOLUENE | 0.604 | | 0.304 | |
| 1,1,1-TRICHLOROETHANE | 0.548 | | 0.287 | |
| TRICHLOROETHYLENE | 0.426 | 0.285 | | |
| M-XYLENE | 0.758 | 0.021 | 0.316 | |
| WATER | | | | 1.000 |
| TRIETHYLAMINE | 0.557 | 0.105 | | |
| 1-OCTANOL | 0.766 | 0.032 | 0.624 | 0.335 |

### Reference

C.-C. Chen and Y. Song, "Solubility Modeling with a Nonrandom Two-Liquid Segment Activity Coefficient Model," *Ind. Eng. Chem. Res.* 43, 8354 (2004).

# Using NRTL-SAC

NRTL-SAC (patent pending) is a segment contribution activity coefficient model, derived from the Polymer NRTL model, usable in Aspen Properties and Aspen Polymers Plus. NRTL-SAC can be used for fast, qualitative estimation of the solubility of complex organic compounds in common solvents. For more information about the model, see NRTL-SAC.

The NRTL-SAC model in the Aspen Physical Property System is a liquid activity coefficient model called **NRTLSAC**. To specify it:

1. On the **Properties | Specifications** sheet, specify an activity coefficient model, such as NRTL.
2. Click the **Properties | Property Methods** folder.
3. In the **Object Manager**, click **New**.
4. In the **Create New ID** dialog box, enter a name for the NRTL-SAC method, such as NRTLSAC.
5. In the **Base Property Method** field, select **NRTL**.
6. Click the **Models** tab.
7. Change the **Model Name** for **GAMMA** from **GMRENON** to **NRTLSAC**.

In order to use NRTL-SAC, all components must be defined as oligomers. Four conceptual segments also must be defined. On the **Components | Polymers | Oligomers** sheet, enter a number for at least one conceptual segment for each oligomer component, as required by the definition of an oligomer. These numbers are not used by NRTL-SAC.

On the **Properties | Parameters | Binary Interaction | NRTL-1** form, enter the binary parameters between conceptual segments. In the following example, the conceptual segments are named **X**, **Y-**, **Y+**, and **Z**.

| Segment 1 | X | X | Y- | Y+ | X |
|---|---|---|---|---|---|
| Segment 2 | Y- | Z | Z | Z | Y+ |
| AIJ | 1.643 | 6.547 | -2.000 | 2.000 | 1.643 |

| Segment 1 | X | X | Y- | Y+ | X |
|-----------|-----|------|------|------|------|
| Segment 2 | Y- | Z | Z | Z | Y+ |
| AJI | 1.834 | 10.949 | 1.787 | 1.787 | 1.834 |
| CIJ | 0.2 | 0.2 | 0.3 | 0.3 | 0.2 |

On the **Properties | Parameters | Binary Interaction | NRTLXY-1** form, enter a non-zero value for at least one of the four parameters for each component.

# 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 systems with any other solvent or mixed solvents.

This section provides theoretical background for the model. All model equations and parameter requirements are included.

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. Henry's law parameters are required for all other components in the aqueous solution. The model development and working equations are provided in the following sections. Parameter conversion between the Pitzer notation and our notation is also provided.

The Pitzer model in the Aspen Physical Property System involves user-supplied parameters that are used in the calculation of binary and ternary parameters for the electrolyte system.

Five elements ($P_1$ through $P_5$) account for the temperature dependencies of parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$, $C^{\varphi}$, $\theta$, and $\Psi$. 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:

| $T^{ref}$ | = | 298.15 K |
|-----------|---|----------|

The user must:

- Supply these elements for the binary parameters using a **Properties | Parameters | Binary | T-Dependent** form.

- Supply these elements for $\Psi$ on the Properties | Parameters | Electrolyte Ternary  form.

- Specify Comp ID $i$ and Comp ID $j$ (and Comp ID $k$ for $\Psi$) on these forms, using the same order that appears on the Components Specifications Selection sheet.

The parameters are summarized in the following table. There is a Pitzer parameter databank in the Aspen Physical Property System (see *Physical Property Data*).

| Parameter Name | Provides P1 - P5 for | 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 | $C^{\varphi}$ | 5 | 0 | x | — |
| **Cation-Cation Parameters** | | | | | |
| GMPTTH | $\theta_{cc'}$ | 5 | 0 | x | — |
| **Anion-Anion Parameters** | | | | | |
| GMPTTH | $\theta_{aa'}$ | 5 | 0 | x | — |
| **Ternary Parameters** | | | | | |
| GMPTPS, GMPTP1, GMPTP2, GMPTP3, GMPTP4 | $\Psi_{ijk}$ | 1 (in each parameter) | 0 | x | — |
| **Molecule-Ion and Molecule-Molecule Parameters** | | | | | |
| GMPTB0 | $\beta^{(0)}$ | 5 | 0 | x | — |
| GMPTB1 | $\beta^{(1)}$ | 5 | 0 | x | — |
| GMPTC | $C^{\varphi}$ | 5 | 0 | x | — |

## Model Development

The Pitzer model analyzes "hard-core" effects in the Debye-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:

$$\frac{G^E}{n_w RT} = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \tag{2}$$

Where:

| | | |
|---|---|---|
| $G^E$ | = | Excess Gibbs energy |
| $R$ | = | Gas constant |
| $T$ | = | Temperature |
| $n_w$ | = | Kilograms of water |
| $m_i$ | = | $\dfrac{x_i}{x_w}\left(\dfrac{M_w}{1000}\right) = \dfrac{n_i}{n_w}$ (molality of ion $i$) |

With:

| | | |
|---|---|---|
| $x_i$ | = | Mole fraction of ion $i$ |
| $x_w$ | = | Mole fraction of water |
| $M_w$ | = | Molecular weight of water (g/mol) |
| $n_i$ | = | Moles of ion $i$ |

The function $f(I)$ is an electrostatic term that expresses the effect of long-range electrostatic forces between ions. This takes into account the hard-core effects of the Debye-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.

In the Aspen Physical Property System, this model is applied using the reference state of infinite dilution solution in water for non-water molecular solutes and ionic species. The properties such as DHAQFM are obtained at 25 C and 1 atm.

## 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:

$$\frac{G^E}{RT} = n_w \left[ f(I) + 2\sum_c\sum_a m_c m_a \left( B_{ca} + \left( \sum_c m_c |z_c| \right) C_{ca} \right) \right.$$
$$+ \sum_c\sum_{c'} m_c m_{c'} \left( \theta_{cc'} + \frac{1}{2}\sum_a m_a \Psi_{cc'a} \right)$$
$$\left. + \sum_a\sum_{a'} m_a m_{a'} \left( \theta_{aa'} + \frac{1}{2}\sum_c m_c \Psi_{caa'} \right) \right]$$

(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 of $\beta^{(0)}$, $\beta^{(2)}$, 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 + $H_2O$ or NaCl + NaNO$_3$ + $H_2O$ (sic, Pitzer, 1989). These terms are discussed in detail later in this section.

Fürst and Renon (1982) propose the following expression as the Pitzer equation for the excess Gibbs energy:

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

(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 $z_j$, 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 $z_j$ =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.

Pitzer (1975) modified his model by adding the electrostatic unsymmetrical mixing effects, producing this modified Pitzer equation for the excess Gibbs energy:

$$\frac{G^E}{RT} = n_w \left[ \begin{array}{l} f(I) + \sum_i \sum_j B_{ij} m_i m_j + \sum_i \sum_j \theta_{ij} m_i m_j + \tfrac{1}{2} \sum_i \sum_j \left( \sum_k m_k |z_k| \right) C_{ij} m_i m_j \\ + \tfrac{1}{6} \sum_i \sum_j \sum_k \Psi_{ijk} m_i m_j m_k + \sum_i \sum_j \Phi_{ij} m_i m_j \end{array} \right] \tag{4a}$$

# Calculation of Activity Coefficients

The natural logarithm of the activity coefficient for ions is calculated from equation 4a to give:

$$\ln \gamma_{m,i}^* = \frac{\partial \left( \dfrac{G^E}{RT} \right)}{\partial n_i}$$

$$= \tfrac{1}{2} z_i^2 f' + 2 \sum_j m_j B_{ij} + \tfrac{1}{2} z_i^2 \sum_j \sum_k B'_{jk} m_j m_k$$

$$+ 2 \sum_j \theta_{ij} m_j + \tfrac{1}{2} |z_i| \sum_j \sum_k C_{jk} m_j m_k$$

$$+ \sum_j \left( \sum_k m_k |z_k| \right) C_{ij} m_j + \tfrac{1}{2} \sum_j \sum_k \Psi_{ijk} m_j m_k$$

$$+ 2 \sum_j m_j \Phi_{ij} + \tfrac{1}{2} z_i^2 \sum_j \sum_k \Phi'_{jk} m_j m_k$$

Where $\theta$ is neglected and $\Phi_{ij}$ and $\Phi'_{ij}$ are the electrostatic unsymmetric mixing effects:

$$\Phi_{ij} = \frac{z_i z_j}{4I} \left[ X_{ij} - \tfrac{1}{2} X_{ii} - \tfrac{1}{2} X_{jj} \right]$$

$$\Phi'_{ij} = \frac{z_i z_j}{8I^2} \left[ X'_{ij} - \tfrac{1}{2} X'_{ii} - \tfrac{1}{2} X'_{jj} \right]$$

The *X* parameters are calculated differently on the option code.

For option code = –1, there is no unsymmetric mixing correction term:

$$X_{ij} = 0$$

$$X'_{ij} = 0$$

For option code = 0 (default), the unsymmetric mixing correction term is in polynomial form:

$$X_{ij} = \frac{X_{ij}^*}{4 + 4.581 X_{ij}^{*(-0.7237)} \exp\left( -0.012 X_{ij}^{*0.528} \right)}$$

$$X'_{ij} = \frac{d(X_{ij})}{dX_{ij}^*}$$

$$X_{ij}^* = 6 A_\phi I^{\frac{1}{2}} z_i z_j$$

For option code = 1, the unsymmetric mixing correction term is in integral form:

$$X_{ij} = \frac{1}{4} X_{ij}^{\bullet} - 1 + \frac{1}{X_{ij}^{\bullet}} \int_0^{\infty} \left\{ 1 - \exp\left[ -\left( \frac{X_{ij}^{\bullet}}{Y} \right) e^{-Y} \right] \right\} Y^2 dY$$

$$X_{ij}' = \frac{d(X_{ij})}{dX_{ij}^{\bullet}}$$

$$X_{ij}^{\bullet} = 6 A_{\varphi} I^{\frac{1}{2}} z_i z_j$$

For water the logarithm of the activity coefficient is calculated similarly, as follows:

Applying:

$$\ln \gamma_{m,w} = \frac{\partial \left( \frac{G^E}{RT} \right)}{\partial n_w}$$

to equation 3 and using:

$$n_w = \frac{N_w M_w}{1000}$$

Where $N_w$ = moles water, gives:

$$\frac{1000}{M_w} \ln \gamma_{m,w} = f - If' - \sum_i \sum_j m_i m_j B_{ij} - \sum_i \sum_j B_{ij}' I - \sum_i \sum_j m_i m_j \theta_{ij}$$
$$- \sum_i \sum_j \Sigma_k m_k |z_k| m_i m_j C_{ij} - \frac{1}{3} \sum_i \sum_j \sum_k m_i m_j m_k \Psi_{ijk}$$

$\quad$ (6)

$f(I)$, the electrostatic term, is expressed as a function of ionic strength $I$ :

$$f(I) = -A_{\varphi} \left( \frac{4I}{b} \right) \left[ \ln \left( 1 + bI^{\frac{1}{2}} \right) \right]$$

$\quad$ (7)

$I$, the ionic strength, is defined as:

$$I = \frac{1}{2} \sum_i m_i z_i^2$$

$\quad$ (8)

Taking the derivative of equation 7 with respect to $I$, gives:

$$f'(I) = \frac{df}{dI} = -2A_{\varphi} \left[ \frac{I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} + \frac{2}{b} \ln \left( 1 + bI^{\frac{1}{2}} \right) \right]$$

$\quad$ (9)

So that:

$$f - If' = \frac{-2A_{\varphi} I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}}$$

$\quad$ (10)

This equation is used in equation 6. In equations 7 and 9, is the usual Debye-Hückel constant for the osmotic coefficient, determined from:

$$A_\varphi = \frac{1}{3}\left(\frac{2\pi N_A d_w}{1000}\right)^{\frac{1}{2}}\left(\frac{Q_e^2}{\varepsilon_B kT}\right)^{\frac{3}{2}}$$

(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 $B$:

$$B = \beta_{ij}^{(0)} + \frac{2\beta_{ij}^{(1)}}{\alpha_1^2 I}\left[1 - \left(1 + \alpha_1 I^{\frac{1}{2}}\right)e^{\left(-\alpha_1 I^{\frac{1}{2}}\right)}\right]$$

(12)

with $\alpha_1 = 2.0$.

For $n$-$m$ electrolytes, $n$ and $m > 1$ (2-2, 2-3, 3-4, and so on), $B$ is determined by the following expression:

$$B = \beta_{ij}^{(0)} + \frac{2\beta_{ij}^{(2)}}{\alpha_2^2 I}\left[1 - \left(1 + \alpha_2 I^{\frac{1}{2}}\right)e^{\left(-\alpha_2 I^{\frac{1}{2}}\right)}\right] + \frac{2\beta_{ij}^{(3)}}{\alpha_3^2 I}\left[1 - \left(1 + \alpha_3 I^{\frac{1}{2}}\right)e^{\left(-\alpha_3 I^{\frac{1}{2}}\right)}\right]$$

(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:

$$B' = \frac{2\beta^{(1)}}{4I^2}\left[-1 + \left(1 + 2I^{\frac{1}{2}} + 2I\right)e^{\left(-2I^{\frac{1}{2}}\right)}\right]$$

(14)

and for $n$-$m$ electrolytes:

$$B' = \frac{2\beta^{(2)}}{144\,I^2}\left[-1 + \left(1 + 12I^{\frac{1}{2}} + 72I\right)e^{\left(-12I^{\frac{1}{2}}\right)}\right]$$

$$+ \frac{2\beta^{(3)}}{(1.4)^2 I^2}\left[-1 + \left(1 + 1.4I^{\frac{1}{2}} + \frac{(1.4)^2 I}{2}\right)e^{\left(-1.4I^{\frac{1}{2}}\right)}\right]$$

(15)

The parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$ and also $C$, $\theta$, and $\Psi$ can be found in Pitzer's articles .

After the activity coefficients are calculated, they can be converted to the mole fraction scale from the molality scale by the following relations:

For solutes:

$$\gamma_{x,i} = \gamma_{m,i}\left(\frac{m_i}{x_i}\right)\left(\frac{M_w}{1000}\right) \qquad (16)$$

For water as a solvent:

$$\gamma_{x,w} = \gamma_{m,i}\left(1 + \frac{\sum\limits_{\substack{i=1 \\ i\neq water}}^{N} x_i}{x_w}\right) \qquad (17)$$

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 the Aspen Physical Property System involves user-supplied parameters. These parameters are used in the calculation of binary and ternary parameters for the electrolyte system. These parameters include the cation-anion parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$ and $C^{\varphi}$, 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, $C^{\varphi}$. The

parameter names in the Aspen Physical Property System and their requirements are discussed in Pitzer Activity Coefficient Model.

## Parameter Conversion

For *n-m* electrolytes, *n* and *m*>1 (2-2, 2-3, 3-4, and so on), the parameter $\beta^{(3)}$ corresponds to Pitzer's $\beta^{(1)}$. $\beta^{(2)}$ is the same in both the Aspen Physical Property System and original Pitzer models. Pitzer refers to the n-m electrolyte parameters as $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(0)}$. $\beta^{(0)}$ and $\beta^{(2)}$ retain their meanings in both models, but Pitzer's $\beta^{(1)}$ is $\beta^{(3)}$ in the Aspen Physical Property System. Be careful to make this distinction when entering n-m electrolyte parameters.

Pitzer often gives values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$, and $C^{\varphi}$ 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:

| | | |
|---|---|---|
| $C_{ca}^{G^{E}}$ | = | $1/2\, C_{ca}^{\phi}$ |
| $n_{a}$ | = | 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 $2(n_{c}n_{a})^{3/2}$.

Aspen Physical Property System accounts for these correcting factors. Enter the parameters without their correcting factors.

For example, Pitzer gives the values of parameters for $MgCl_2$ as:

| | | |
|---|---|---|
| $4/3\,\beta^{(0)}$ | = | 0.4698 |
| $4/3\,\beta^{(1)}$ | = | 2.242 |
| $\dfrac{2^{5/2}}{3}C^{\phi}$ | = | 0.00979 |

Perform the necessary conversions and enter the parameters as:

| | | |
|---|---|---|
| $\beta^{(0)}_{Mg^{2+},Cl^{-}}$ | = | 0.3524 |
| $\beta^{(0)}_{Mg^{2+},Cl^{-}}$ | = | 1.6815 |
| $C^{\phi}_{Mg^{2+},Cl^{-}}$ | = | 0.00520 |

# Parameter Sources

Binary and ternary parameters for the Pitzer model for various electrolyte systems are available from Pitzer's series on the thermodynamics of electrolytes. These papers and the electrolyte parameters they give are:

| Reference | Parameters available |
|---|---|
| (Pitzer, 1973) | Binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $C^{\phi}$) 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 |
| (Silvester and Pitzer, 1977) | Data for NaCl and aqueous NaCl solutions |
| (Pitzer, Silvester, and Peterson, 1978) | Rare earth chlorides, nitrates, and perchlorates |
| (Peiper and Pitzer, 1982) | Aqueous carbonate solutions, including mixtures of sodium carbonate, bicarbonate, and chloride |
| (Phutela and Pitzer, 1983) | Aqueous calcium chloride |
| (Conceicao, de Lima, and Pitzer, 1983) | Saturated aqueous solutions, including mixtures of sodium chloride, potassium chloride, and cesium chloride |
| (Pabalan and Pitzer, 1987) | Parameters for polynomial unsymmetric mixing term |
| (Kim and Frederick, 1988) | Parameters for integral unsymmetric mixing term |

# Pitzer References

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Phutela, R.C. and K.S. Pitzer, "Thermodynamics of Aqueous Calcium Chloride," *J. Solution Chem.*, Vol. 12, No. 3, (1983), pp. 201-207.

Pitzer, K.S., "Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations, " *J. Phys. Chem.,* Vol. 77, No. 2, (1973), pp. 268-277.

Pitzer, K.S., *J. Solution Chem.,* Vol. 4, (1975), p. 249.

Pitzer, K.S., "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).

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Pitzer, K.S. and G. Mayorga, *J. Solution Chem.,* Vol. 3, (1974), p. 539.

Pitzer, K.S., 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.

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Silvester, L.F. 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.

# Polynomial Activity Coefficient

This model represents activity coefficient 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:

$$\gamma_i = f_i$$

This model is not part of any property method. To use it:

1. On the **Properties | Specifications** sheet, specify an activity coefficient model, such as NRTL.
2. Click the **Properties | Property Methods** folder.
3. In the **Object Manager**, click **New**.
4. In the **Create New ID** dialog box, enter a name for the new method.
5. In the **Base Property Method** field, select **NRTL**.
6. Click the **Models** tab.
7. Change the **Model Name** for **GAMMA** from **GMRENON** to **GMPOLY**.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| GMPLYP/1 | $a_{i1}$ | 0 | X | — | — | — |
| GMPLYP/2 | $a_{i2}$ | 0 | X | — | — | — |
| GMPLYP/3 | $a_{i3}$ | 0 | X | — | — | — |
| GMPLYP/4 | $b_{i1}$ | 0 | X | — | — | — |
| GMPLYP/5 | $b_{i2}$ | 0 | X | — | — | — |
| GMPLYP/6 | $b_{i3}$ | 0 | X | — | — | — |
| GMPLYP/7 | $c_{i1}$ | 0 | X | — | — | — |
| GMPLYP/8 | $c_{i2}$ | 0 | X | — | — | — |
| GMPLYP/9 | $c_{i3}$ | 0 | X | — | — | — |
| GMPLYP/10 | $d_{i1}$ | 0 | X | — | — | — |
| GMPLYP/11 | $d_{i2}$ | 0 | X | — | — | — |
| GMPLYP/12 | $d_{i3}$ | 0 | X | — | — | — |
| GMPLYP/13 | $e_{i1}$ | 0 | X | — | — | — |
| GMPLYP/14 | $e_{i2}$ | 0 | X | — | — | — |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| GMPLYP/15 | $e_{i3}$ | 0 | x | — | — | — |
| GMPLYO | $f_i$ | — | x | — | — | — |

**Note:** If you specify GMPLYP on the **Properties | Parameters | Pure Component | T-Dependent** sheet, you can only enter the first 12 elements. If you want to specify values for elements 13 to 15, you should go to the **Flowsheeting Options | Add-Input | Add After** sheet in Aspen Plus or the **Add-Input | Add-Input | Add After** sheet in Aspen Properties, and enter the values of all 15 elements as in the following example:

```
PROP-DATA GMPLYP-1
    IN-UNITS SI
    PROP-LIST GMPLYP
    PVAL WATER 0.0 1.5 0.0 &
               0.0 0.0 0.0 &
               0.0 0.0 0.0 &
               0.0 0.0 0.0 &
               0.0 16. 0.0
```

# 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:

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

Where:

| | | |
|---|---|---|
| $nc$ | = | Number of components |
| $A_{1,ij}$ | = | $a_{ij} / T + b_{ij}$ |
| $A_{2,ij}$ | = | $c_{ij} / T + d_{ij}$ |
| $A_{3,ij}$ | = | $e_{ij} / T + f_{ij}$ |
| $A_{4,ij}$ | = | $g_{ij} / T + h_{ij}$ |
| $A_{5,ij}$ | = | $m_{ij} / T + n_{ij}$ |
| $A_{n,ii}$ | = | $A_{n,ii} = 0.0$ |
| $A_{n,ji}$ | = | $A_{n,ij}(-1)^{(n-1)}$ |
| $A_{n,ki}$ | = | $A_{n,ik}(-1)^{(n-1)}$ |

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

$\gamma_i = v_i$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| GMRKTB/1 | $a_{ij}$ | 0 | x | — | — | — |
| GMRKTB/2 | $b_{ij}$ | 0 | x | — | — | — |
| GMRKTB/3 | $c_{ij}$ | 0 | x | — | — | — |
| GMRKTB/4 | $d_{ij}$ | 0 | x | — | — | — |
| GMRKTB/5 | $e_{ij}$ | 0 | x | — | — | — |
| GMRKTB/6 | $f_{ij}$ | 0 | x | — | — | — |
| GMRKTB/7 | $g_{ij}$ | 0 | x | — | — | — |
| GMRKTB/8 | $h_{ij}$ | 0 | x | — | — | — |
| GMRKTB/9 | $m_{ij}$ | 0 | x | — | — | — |
| GMRKTB/10 | $n_{ij}$ | 0 | x | — | — | — |
| GMRKTO | $v_i$ | — | x | — | — | — |

# Scatchard-Hildebrand

The Scatchard-Hildebrand model calculates liquid activity coefficients. It is used in the CHAO-SEA property method and the GRAYSON property method.

The equation for the Scatchard-Hildebrand model is:

$$\ln \gamma_i = \frac{V_i^{*,l}}{RT} \sum_j \sum_k \varphi_j \varphi_k \left( A_{ji} - 1/2 \, A_{jk} \right)$$

Where:

| | | |
|---|---|---|
| $A_{ij}$ | = | $\left( \delta_i - \delta_j \right)^2 + 2 k_{ij} \delta_i \delta_j$ |
| $\varphi_i$ | = | $\dfrac{x_i V_i^{*,l}}{V_m^l}$ |
| $V_m^{*,l}$ | = | $\sum_i x_i V_i^{*,l}$ |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper 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 | $V_i^{*,l}$ | $V_i^{*,l} = V_i^{*,CVT}$ $5.7 + 3.0 \left( \dfrac{298.15}{T_{ci}} \right)$ | x | 0.01 | 1.0 | MOLE-VOLUME |
| GMSHXL | $k_{ij}$ | 0.0 | x | -5 | 5 | — |

# 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:

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

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 | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| GMMRGB/1 | $a_{ij}$ | 0 | x | — | — | TEMPERATURE |
| GMMRGB/2 | $b_{ij}$ | 0 | x | — | — | — |
| GMMRGB/3 | $c_{ij}$ | 0 | x | — | — | — |
| GMMRGO | $d_i$ | — | x | — | — | — |

## References

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D.A. Gaskell, Introduction to Metallurgical Thermodyanics, 2nd ed., (New York: Hemisphere Publishing Corp., 1981), p. 360.

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

# UNIFAC Activity Coefficient Model

The UNIFAC model calculates liquid activity coefficients for the following property methods: UNIFAC, UNIF-HOC, and UNIF-LL. Because the UNIFAC model is a group-contribution model, it is predictive. All published group parameters and group binary parameters are stored in the Aspen Physical Property System.

The equation for the original UNIFAC liquid activity coefficient model is made up of a combinatorial and residual term:

| $\ln \gamma$ | = | $\ln \gamma_i^c + \ln \gamma_i^r$ |
|---|---|---|
| $\ln \gamma_i^c$ | = | $\ln\left(\dfrac{\Phi_i}{x_i}\right) + 1 - \dfrac{\Phi_i}{x_i} - \dfrac{Z}{2}\left[\ln \dfrac{\Phi_i}{\theta_i} + 1 - \dfrac{\Phi_i}{\theta_i}\right]$ |

Where the molecular volume and surface fractions are:

$$\Phi_i = \frac{x_i r_i}{\sum\limits_{j}^{nc} x_j r_j} \qquad \theta_i = \frac{x_i \frac{z}{2} q_i}{\sum\limits_{j}^{nc} x_j \frac{z}{2} q_j}$$

and

Where nc is the number of components in the mixture. The coordination number $z$ is set to 10. The parameters $r_i$ and $q_i$ are calculated from the group volume and area parameters:

$$r_i = \sum\limits_{k}^{ng} v_{ki} R_k \qquad q_i = \sum\limits_{k}^{ng} v_{ki} Q_k$$

and

Where $v_{ki}$ is the number of groups of type $k$ in molecule $i$, and $ng$ is the number of groups in the mixture.

The residual term is:

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

$\Gamma_k$ 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:

$$\ln \Gamma_k = Q_k \left(1 - \ln \sum\limits_{m}^{ng} \theta_m \tau_{mk} - \sum\limits_{m}^{ng} \frac{\theta_m \tau_{km}}{\sum\limits_{n}^{ng} \theta_n \tau_{nm}}\right)$$

With:

$$\theta_k = \frac{X_k \frac{z}{2} Q_k}{\sum\limits_{m}^{ng} X_m \frac{z}{2} Q_m}$$

And:

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

The parameter $X_k$ is the group mole fraction of group $k$ in the liquid:

$$X_k = \frac{\sum\limits_{j}^{nc} v_{kj} x_j}{\sum\limits_{j}^{nc} \sum\limits_{m}^{ng} v_{mj} x_j}$$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| UFGRP | $(k, v_k, m, v_m, ...)$ | — | — | — | — | — |
| GMUFQ | $Q_k$ | — | — | — | — | — |
| GMUFR | $R_k$ | — | — | — | — | — |
| GMUFB | $b_{kn}$ | — | — | — | — | TEMPERATURE |

The parameter UFGRP stores the UNIFAC functional group number and number of occurrences of each group. UFGRP is stored in the Aspen Physical Property System pure component databank for most components. For nondatabank components, enter UFGRP on the Properties Molecular Structure Functional Group sheet. See *Physical Property Data*, Chapter 3, for a list of the UNIFAC functional groups.

### References

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

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

H.K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, "Vapor-Liquid Equilibria by UNIFAC Group Contribution. 5 Revision and Extension", Ind. Eng. Chem. Res., Vol. 30, (1991), pp. 2352-2355.

# UNIFAC (Dortmund Modified)

The UNIFAC modification by Gmehling and coworkers (Weidlich and Gmehling, 1987; Gmehling et al., 1993), is slightly different in the combinatorial part. It is otherwise unchanged compared to the original UNIFAC:

$$\ln \gamma_i^c = \ln\left(\frac{\Phi_i'}{x_i}\right) + 1 - \frac{\Phi_i}{x_i} - \frac{z}{2}q_i\left(\ln\frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i}\right)$$

With:

$$\frac{\Phi_i'}{x_i} = \frac{r_i^{\frac{3}{4}}}{\sum_j x_j r_j^{\frac{3}{4}}}$$

The temperature dependency of the interaction parameters is:

$$a_{mn} = a_{mn,1} + a_{mn,2}T + a_{mn,3}T^2$$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| UFGRPD | $(k, v_k, m, v_m, ...)$ | — | — | — | — | — |
| GMUFDQ | $Q_k$ | — | — | — | — | — |
| GMUFDR | $R_k$ | — | — | — | — | — |
| UNIFDM/1 | $a_{mn,1}$ | 0 | — | — | — | TEMPERATURE |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| UNIFDM/2 | $a_{mn.2}$ | 0 | — | — | — | TEMPERATURE |
| UNIFDM/3 | $a_{mn.3}$ | 0 | — | — | — | TEMPERATURE |

The parameter UFGRPD stores the group number and the number of occurrences of each group. UFGRPD is stored in the Aspen Physical Property System pure component databank. For nondatabank components, enter UFGRPD on the Properties Molecular Structure Functional Group sheet. See *Physical Property Data*, Chapter 3, for a list of the Dortmund modified UNIFAC functional groups.

## 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:

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

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

The temperature dependency of a is described by a function instead of a constant:

$$a_{mn} = a_{mn,1} + a_{mn,2}(T - 298.15) + a_{mn,3}\left( T\ln\frac{298.15}{T} + T - 298.15 \right)$$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| UFGRPL | $(k, V_k, m, V_m, ...)$ | — | — | — | — | — |
| GMUFLQ | $Q_k$ | — | — | — | — | — |
| GMUFLR | $R_k$ | — | — | — | — | — |
| UNIFLB/1 | $a_{mn,1}$ | 0 | — | — | — | TEMPERATURE |
| UNIFLB/2 | $a_{mn,2}$ | 0 | — | — | — | TEMPERATURE |
| UNIFLB/3 | $a_{mn,3}$ | 0 | — | — | — | TEMPERATURE |

The parameter UFGRPL stores the modified UNIFAC functional group number and the number of occurrences of each group. UFGRPL is stored in the Aspen Physical Property System pure component databank. For nondatabank components, enter UFGRP on the **Properties | Molecular Structure | Functional Group** sheet. See *Physical Property Data*, Chapter 3, for a list of the Larsen modified UNIFAC functional groups.

Reference: 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 Activity Coefficient Model

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:

$$\ln \gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i} - q_i'\ln t_i' - q_i'\sum_j \theta_j'\tau_{ij}\Big/ t_j' + l_i + q_i' - \frac{\Phi_i}{x_i}\sum_j x_j l_j$$

Where:

| | | |
|---|---|---|
| $\theta_i$ | = | $q_i x_i \big/ q_T \; ; \; q_T = \sum_k q_k x_k$ |
| $\theta_i'$ | = | $q_i' x_i \big/ q_T' \; ; \; q_T' = \sum_k q_k' x_k$ |
| $\Phi_i$ | = | $\Phi_i = r_i x_i \big/ r_T \; ; \; r_T = \sum_k r_k x_k$ |
| $l_i$ | = | $\frac{z}{2}(r_i - q_i) + 1 - r_i$ |
| $t_i'$ | = | $\sum_k \theta_k'\tau_{ki}$ |
| $\tau_{ij}$ | = | $\exp(a_{ij} + b_{ij}/T + C_{ij}\ln T + d_{ij}T + e_{ij}/T^2)$ |
| $z$ | = | 10 |

$a_{ij}$, $b_{ij}$, $c_{ij}$, and $d_{ij}$ are unsymmetrical. That is, $a_{ij}$ may not be equal to $a_{ji}$, etc.

Absolute temperature units are assumed for the binary parameters $a_{ij}$, $b_{ij}$, $c_{ij}$, $d_{ij}$, and $e_{ij}$.

can be determined from VLE and/or LLE data regression. The Aspen Physical Property System has a large number of built-in parameters for the UNIQUAC model. The binary parameters have been regressed using VLE and LLE data from the Dortmund Databank. The binary parameters for VLE applications were regressed using the ideal gas, Redlich-Kwong, and Hayden-O'Connell equations of state. See *Physical Property Data*, Chapter 1, for details.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| GMUQR | $r_i$ | — | x | — | — | — |
| GMUQQ | $q_i$ | — | x | — | — | — |
| GMUQQ1 | $q_i'$ | $q$ | x | — | — | — |
| UNIQ/1 | $a_{ij}$ | 0 | x | -50.0 | 50.0 | — |
| UNIQ/2 | $b_{ij}$ | 0 | x | -15000.0 | 15000.0 | TEMPERATURE |
| UNIQ/3 | $c_{ij}$ | 0 | x | — | — | TEMPERATURE |
| UNIQ/4 | $d_{ij}$ | 0 | x | — | — | TEMPERATURE |
| UNIQ/5 | $T_{lower}$ | 0 K | x | — | — | TEMPERATURE |
| UNIQ/6 | $T_{upper}$ | 1000 K | x | — | — | TEMPERATURE |
| UNIQ/7 | $e_{ij}$ | 0 | x | — | — | TEMPERATURE |

Absolute temperature units are assumed for elements 2 through 4 and 7 of UNIQ.

The UNIQ-2 property method uses data set 2 for UNIQ. All other UNIQUAC methods use data set 1.

## 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 Activity Coefficient Model

The Van Laar model (Van Laar 1910) calculates liquid activity coefficients for the property methods: VANLAAR, VANL-2, VANL-HOC, VANL-NTH, and VANL-RK. It can be used for highly nonideal systems.

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

Where:

| | | |
|---|---|---|
| $z_i$ | = | $\dfrac{|A_i|x_i}{|A_i|x_i+|B_i|(1-x_i)}$ |
| $A_i$ | = | $\sum_j x_j A_{ij}/(1-x_i)$ |
| $B_i$ | = | $\sum_j x_j A_{ji}/(1-x_i)$ |
| $C_i$ | = | $\sum_j x_j C_{ij}/(1-x_i)$ |
| $A_{ij}$ | = | $a_{ij}+b_{ij}/T$ |
| $C_{ij}$ | = | $c_{ij}+d_{ij}/T$ |
| $C_{ii}$ | = | $C_{ji}$ |
| $A_{ii}$ | = | $B_{ii}=C_{ii}=0$ |

$a_{ij}$ and $b_{ij}$ are unsymmetrical. That is, $a_{ij}$ may not be equal to $a_{ji}$, and $b_{ij}$ may not be equal to $b_{ji}$.

| 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 |

The VANL-2 property method uses data set 2 for VANL. All other Van Laar methods use data set 1.

## 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. Bale, "A Modified Interaction Parameter Formalism for Non-Dilute Solutions," Metallurgical Transactions A, Vol. 17A, (July 1986), p. 1211.

# Wilson Activity Coefficient Model

The Wilson model calculates liquid activity coefficients for the following property methods: WILSON, WILS2, WILS-HOC, WILS-NTH, WILS-RK, WILS-HF, WILS-LR, and WILS-GLR. It is recommended for highly nonideal systems, especially alcohol-water systems. It can also be used in the advanced equation-of-state mixing rules, such as Wong-Sandler and MHV2. This model cannot be used for liquid-liquid equilibrium calculations.

The equation for the Wilson model is:

$$\ln \gamma_i = 1 - \ln\left(\sum_j A_{ij} x_j\right) - \sum_j \frac{A_{ji} x_j}{\sum_k A_{jk} x_k}$$

Where:

| | | | |
|---|---|---|---|
| $\ln A_{ij}$ | = | $a_{ij} + b_{ij}/T + c_{ij} \ln T + d_{ij} T + e_{ij}/T^2$ | † |

The extended form of $\ln A_{ij}$ provides more flexibility in fitting phase equilibrium and enthalpy data. $a_{ij}$, $b_{ij}$, $c_{ij}$, $d_{ij}$, and $e_{ij}$ are unsymmetrical. That is, $a_{ij}$ may not be equal to $a_{ji}$, etc.

The binary parameters $a_{ij}$, $b_{ij}$, $c_{ij}$, $d_{ij}$, and $e_{ij}$ must be determined from data regression or VLE and/or heat-of-mixing data. The Aspen Physical Property System has a large number of built-in binary parameters for the Wilson model. The binary parameters have been regressed using VLE data from the Dortmund Databank. The binary parameters were regressed using the ideal gas, Redlich-Kwong, and Hayden-O'Connell equations of state. See *Physical Property Data*, Chapter 1, for details.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| WILSON/1 | $a_{ii}$ | 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 †† |
| WILSON/5 | $T_{lower}$ | 0 K | x | — | — | TEMPERATURE |
| WILSON/6 | $T_{upper}$ | 1000 K | x | — | — | TEMPERATURE |
| WILSON/7 | $e_{ij}$ | 0 | x | — | — | TEMPERATURE †† |

The WILS-2 property method uses data set 2 for WILSON. All other Wilson methods use data set 1.

† In the original formulation of the Wilson model, $a_{ij} = \ln V_j/V_i$, $c_{ij} = d_{ij} = e_{ij} = 0$, and

$b_{ij} = -(\lambda_{ij} - \lambda_{ii})/R$, where $V_j$ and $V_i$ are pure component liquid molar volume at 25°C.

†† If any of $b_{iA}$, $c_{iA}$, and $e_{iA}$ are non-zero, absolute temperature units are assumed for all coefficients. If $b_{iA}$, $c_{iA}$, and $e_{iA}$ are all zero, the others are interpreted in input units. The temperature limits are always interpreted in input units.

### References

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

# Wilson Model with Liquid Molar Volume

This Wilson model (used in the method WILS-VOL) 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:

| | | |
|---|---|---|
| $\ln A_{ij}$ | $=$ | $\ln V_j/V_i + a_{ij} + b_{ij}/T + c_{ij}\ln T + d_{ij}T + e_{ij}/T^2$ † |

$V_j$ and $V_i$ are pure component liquid molar volume at the system temperature calculated using the Rackett/DIPPR/IK-CAPE model. The extended form of $\ln A_{ij}$ provides more flexibility in fitting phase equilibrium and enthalpy data. $a_{ij}$, $b_{ij}$, $c_{ij}$, $d_{ij}$, and $e_{ij}$ are unsymmetrical. That is, $a_{ij}$ may not be equal to $a_{ji}$, etc.

The binary parameters $a_{ij}$, $b_{ij}$, $c_{ij}$, $d_{ij}$, and $e_{ij}$ must be determined from data regression of VLE and/or heat-of-mixing data. There are no built in binary parameters for this model.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| WSNVOL/1 | $a_{ii}$ | 0 | x | -50.0 | 50.0 | — |
| WSNVOL/2 | $b_{ij}$ | 0 | x | -15000.0 | 15000.0 | TEMPERATURE †† |
| WSNVOL/3 | $c_{ij}$ | 0 | x | -— | — | TEMPERATURE †† |
| WSNVOL/4 | $d_{ij}$ | 0 | x | — | — | TEMPERATURE †† |
| WSNVOL/5 | $e_{ij}$ | 0 | x | — | — | TEMPERATURE †† |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| WSNVOL/6 | $T_{lower}$ | 0 K | x | — | — | TEMPERATURE |
| WSNVOL/7 | $T_{upper}$ | 1000 K | x | — | — | TEMPERATURE |

Pure component parameters for the Rackett model/DIPPR/IK-CAPE are also required.

† In the original formulation of the Wilson model, $a_{ij} = c_{ij} = d_{ij} = e_{ij} = 0$ and

$$b_{ij} = -\frac{(\lambda_{ij} - \lambda_{ii})}{R}$$

. $V_j$ and $V_i$ are calculated at 25°C.

†† If any of $b_{iA}$, $c_{iA}$, and $e_{iA}$ are non-zero, absolute temperature units are assumed for all coefficients. If $b_{iA}$, $c_{iA}$, and $e_{iA}$ are all zero, the others are interpreted in input units. The temperature limits are always interpreted in input units.

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

# Vapor Pressure and Liquid Fugacity Models

The Aspen Physical Property System has the following 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 |
| API Sour | Vapor pressure |
| Braun K-10 | Vapor pressure |
| Chao-Seader | Fugacity |
| Grayson-Streed | Fugacity |
| Kent-Eisenberg | Fugacity |
| Maxwell-Bonnell | Vapor pressure |
| Solid Antoine | Vapor pressure |

## Extended Antoine/Wagner/PPDS/IK-CAPE Liquid Vapor Pressure Model

The Aspen Physical Property System has several submodels for calculating vapor pressure of a liquid. It uses parameter THRSWT/3 to determine which submodel is used. See Pure Component Temperature-Dependent Properties for details.

| If THRSWT/3 is | Then this equation is used |
|---|---|
| 0 | Extended Antoine |
| 200 | BARIN |

| If THRSWT/3 is | Then this equation is used |
|---|---|
| 301 | Wagner |
| 302 | PPDS Modified Wagner |
| 400 | PML |
| 401 | IK-CAPE |
| 501 | NIST TDE Polynomial |
| 502 | NIST Wagner 25 |

## Extended Antoine Equation

Parameters for many components are available for the extended Antoine equation from the Aspen Physical Property System pure component databank. This equation can be used whenever the parameter PLXANT is available.

The equation for the extended Antoine vapor pressure model is:

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

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 | $C_{3i}$, ..., $C_{7i}$ | 0 | x | | | TEMPERATURE |
| PLXANT/8 | $C_{8i}$ | 0 | x | | | TEMPERATURE |
| PLXANT/9 | $C_{9i}$ | 1000 | x | | | TEMPERATURE |

If $C_{5i}$, $C_{6i}$, or $C_{7i}$ is non-zero, absolute temperature units are assumed for all coefficients $C_{1i}$ through $C_{7i}$. The temperature limits are always in user input units.

## Wagner Vapor Pressure Equation

The Wagner vapor pressure equation is the best equation for correlation. The equation can be used if the parameter WAGNER is available:

$$\ln p_{ri}^{*,l} = \left(C_{1i}\left(1-T_{ri}\right) + C_{2i}\left(1-T_{ri}\right)^{1.5} + C_{3i}\left(1-T_{ri}\right)^3 + C_{4i}\left(1-T_{ri}\right)^6\right)\Big/T_{ri} \ \text{for}\ C_{5i} \leq T \leq C_{6i}$$

Where:

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

$p_{ri}^{*,l} = p_i^{*,l} / p_{ci}$

Linear extrapolation of $\ln p_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

## PPDS Modified Wagner Vapor Pressure Equation

The PPDS equation also uses the same parameter WAGNER as the standard Wagner equation:

$$\ln p_{ri}^{*,l} = \left( C_{1i}\left(1 - T_{ri}\right) + C_{2i}\left(1 - T_{ri}\right)^{1.5} + C_{3i}\left(1 - T_{ri}\right)^{2.5} + C_{4i}\left(1 - T_{ri}\right)^{5} \right)\Big/ T_{ri} \text{ for } C_{5i} \leq T \leq C_{6i}$$

Where:

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

$p_{ri}^{*,l} = p_i^{*,l} / p_{ci}$

Linear extrapolation of ln $p_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

| 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 | | | |
| WAGNER/5 | $C_{5i}$ | 0 | x | | | TEMPERATURE |
| WAGNER/6 | $C_{6i}$ | 1000 | x | | | TEMPERATURE |
| TC | $T_{ci}$ | | | | | TEMPERATURE |
| PC | $p_{ci}$ | | | | | PRESSURE |

## NIST Wagner 25 Liquid Vapor Pressure Equation

This equation is the same as the PPDS Modified Wagner equation above, but it uses parameter WAGNER25 instead of WAGNER, and it uses critical properties from this parameter set also.

$$\ln p_i^{*,l} = \ln p_{ci} + \left( C_{1i}\left(1 - T_{ri}\right) + C_{2i}\left(1 - T_{ri}\right)^{1.5} + C_{3i}\left(1 - T_{ri}\right)^{2.5} + C_{4i}\left(1 - T_{ri}\right)^{5} \right)\Big/ T_{ri}$$

$$\text{for } T_{lower} \leq T \leq T_{upper}$$

Where:

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

Linear extrapolation of ln $p_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| WAGNER25/1 | $C_{1i}$ | | x | | | |
| WAGNER25/2 | $C_{2i}$ | 0 | x | | | |
| WAGNER25/3 | $C_{3i}$ | 0 | x | | | |
| WAGNER25/4 | $C_{4i}$ | 0 | x | | | |
| WAGNER25/5 | ln $p_{ci}$ | 0 | x | | | |
| WAGNER25/6 | $T_{ci}$ | | x | | | TEMPERATURE |

2 **Thermodynamic Property Models**

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| WAGNER25/7 | $T_{lower}$ | 0 | x | | | TEMPERATURE |
| WAGNER25/8 | $T_{upper}$ | 1000 | x | | | TEMPERATURE |

## IK-CAPE Vapor Pressure Equation

The IK-CAPE model is a polynomial equation. If the parameter PLPO is available, the Aspen Physical Property System can use the IK-CAPE vapor pressure equation:

$$\ln p_i^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

$$\text{for } C_{11i} \leq T \leq C_{12i}$$

Linear extrapolation of $\ln p_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

| 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 |

## PML Vapor Pressure Equations

The PML vapor pressure equations are modified versions of the Antoine and Wagner equations. Each equation comes in two alternate forms, identical except for the use of natural or base-10 logarithms. Parameter LNVPEQ/1 specifies the number of the equation used. Each equation uses a separate parameter: LNVP1 for equation 1, LOGVP1 for 2, LNPR1 for 3, LOGPR1 for 4, LNPR2 for 5, and LOGPR2 for 6.

Equation 1 (natural logarithm) and 2 (base 10 logarithm):

$$\log p_i^{*,l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}\log T + C_{5i}T + C_{6i}T^2 + C_{7i}T^{C_{8i}}$$

Equation 3 (natural logarithm) and 4 (base 10 logarithm):

$$\log p_{ri}^{*,l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}\log T + C_{5i}T + C_{6i}T^2 + C_{7i}T^{C_{8i}}$$

Equation 5 (natural logarithm) and 6 (base 10 logarithm):

$$\log p_{ri}^{*,l} = \frac{-C_{1i}}{T_{ri}}\left[1 - T_{ri}^2 + C_{2i}\left(3 + T_{ri}\right)\left(1 - T_{ri}\right)^3\right]$$

Where:

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

$p_{ri}^{*,l} = p_i^{*,l} / p_{ci}$

LNVPEQ/2 and LNVPEQ/3 are the lower and upper temperature limits, respectively.

In equations 1-4, if elements 4, 7, or 8 are non-zero, absolute temperature units are assumed for all elements.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| LNVP1/1, ...,8 | $C_{1i}, ..., C_{8i}$ | | x | | | PRESSURE TEMPERATURE |
| LOGVP1/1, ..., 8 | $C_{1i}, ..., C_{8i}$ | | x | | | PRESSURE TEMPERATURE |
| LNPR1/1, ..., 8 | $C_{1i}, ..., C_{8i}$ | | x | | | PRESSURE TEMPERATURE |
| LOGPR1/1, ..., 8 | $C_{1i}, ..., C_{8i}$ | | x | | | PRESSURE TEMPERATURE |
| LNPR2/1,2 | $C_{1i}, C_{2i}$ | | x | | | |
| LOGPR2/1,2 | $C_{1i}, C_{2i}$ | | x | | | |
| LNVPEQ/1 | (equation number) | | | | | |
| LNVPEQ/2 | $T_{lower}$ | 0 | X | | | TEMPERATURE |
| LNVPEQ/3 | $T_{upper}$ | 1000 | X | | | TEMPERATURE |
| TC | $T_{ci}$ | | | | | TEMPERATURE |
| PC | $p_{ci}$ | | | | | PRESSURE |

## NIST TDE Polynomial for Liquid Vapor Pressure

This equation can be used for calculating vapor pressure when parameter PLTDEPOL is available.

$$\ln p_i^{*,l} = C_{1i} + C_{2i}/T + C_{3i}\ln(T) + C_{4i}T + C_{5i}T^2 + C_{6i}/T^2 + C_{7i}T^6 + C_{8i}/T^4$$
$$\text{for } T_{lower} \leq T \leq T_{upper}$$

Linear extrapolation of $\ln p_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

If elements 2, 3, 6, or 8 are non-zero, absolute temperature units are assumed for all elements.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| PLTDEPOL/1 | $C_{1i}$ | | X | | | |
| PLTDEPOL/2 | $C_{2i}$ | 0 | X | | | TEMPERATURE |
| PLTDEPOL/3 | $C_{3i}$ | 0 | X | | | |
| PLTDEPOL/4, ..., 8 | $C_{4i}, ..., C_{8i}$ | 0 | X | | | TEMPERATURE |
| PLTDEPOL/9 | $T_{lower}$ | 0 | X | | | TEMPERATURE |
| PLTDEPOL/10 | $T_{upper}$ | 1000 | X | | | TEMPERATURE |

### References

Reid, Prausnitz, and Poling, *The Properties of Gases and Liquids*, 4th ed., (New York: McGraw-Hill, 1987).

Harlacher and Braun, "A Four-Parameter Extension of the Theorem of Corresponding States," *Ind. Eng. Chem. Process Des. Dev.*, Vol. 9, (1970), p. 479.

W. Wagner, *Cryogenics*, Vol. 13, (1973), pp. 470-482.

D. Ambrose, M. B. Ewing, N. B. Ghiassee, and J. C. Sanchez Ochoa "The ebulliometric method of vapor-pressure measurement: vapor pressures of benzene, hexafluorobenzene, and naphthalene," *J. Chem. Thermodyn.* 22 (1990), p. 589.

# API Sour Model

The API Sour model is based on the API sour water model for correlating the ammonia, carbon dioxide, and hydrogen sulfide volatilities from aqueous sour water system. The model assumes aqueous phase chemical equilibrium reactions involving $CO_2$, $H_2S$, and $NH_3$.

The model is applicable from 20 C to 140 C. The authors developed the model using available phase equilibrium data and reported average errors between the model and measured partial pressure data as follows

| Compound | Average Error, % | |
|---|---|---|
| | Up to 60 C | Above 60 C |
| Ammonia | 10 | 36 |
| Carbon dioxide | 11 | 24 |
| Hydrogen sulfide | 12 | 29 |

Detail of the model is described in the reference below and is too involved to be reproduced here.

### Reference

New Correlation of NH3, CO2, and H2S Volatility Data from Aqueous Sour Water Systems, API Publication 955, March 1978 (American Petroleum Institute).

# Braun K-10 Model

The BK10 model uses the Braun K-10 K-value correlations, which were developed from the K10 charts (K-values at 10 psia) for both real and pseudo components. The form of the equation used is an extended Antoine vapor pressure equation with coefficients specific to real components and pseudo component boiling ranges.

This method is strictly applicable to heavy hydrocarbons at low pressures. However, our model includes coefficients for a large number of hydrocarbons and light gases. For pseudocomponents the model covers boiling ranges 450

– 700 K (350 – 800F). Heavier fractions can also be handled using the methods developed by AspenTech.

### References

B.C. Cajander, H.G. Hipkin, and J.M. Lenoir, "Prediction of Equilibrium Ratios from Nomograms of Improved Accuracy," Journal of Chemical Engineering Data, vol. 5, No. 3, July 1960, p. 251-259.

J.M. Lenoir, "Predict K Values at Low Temperatures, part 1," Hydrocarbon Processing, p. 167, September 1969.

J.M. Lenoir, "Predict K Values at Low Temperatures, part 2," Hydrocarbon Processing, p. 121, October 1969.

# Chao-Seader Pure Component Liquid Fugacity Model

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:

$$\ln \varphi_i^{*,l} = \ln v_i^{(0)} + \omega_i \ln v_i^{(1)}$$

Where:

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

| 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 Pure Component Liquid Fugacity Model

The Grayson-Streed model calculates pure component fugacity coefficients for liquids, and is used in the GRAYSON/GRAYSON2 property methods. It is an empirical model with the Curl-Pitzer form. The general form of the model is:

$$\ln \varphi_i^{*,l} = \ln v_i^{(0)} + \omega_i \ln v_i^{(1)}$$

Where:

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

| 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 Liquid Fugacity Model

The Kent-Eisenberg model calculates liquid mixture component fugacity coefficients and liquid enthalpy for the AMINES property method.

The chemical equilibria in $H_2S$ + $CO_2$ + amine systems are described using these chemical reactions:

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

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

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

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

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

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

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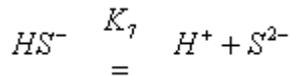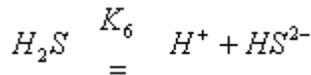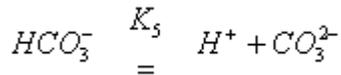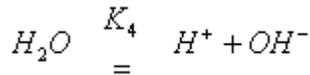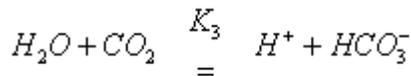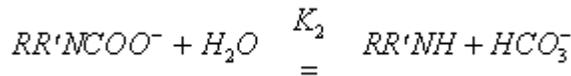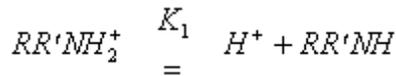
Where:

| | | |
|---|---|---|
| $R'$ | = | Alcohol substituted alkyl groups |

The equilibrium constants are given by:

$$\ln K_i = A_{1i} + A_{2i}/T + A_{3i}/T^2 + A_{4i}/T^3 + A_{5i}/T^4$$

The chemical equilibrium equations are solved simultaneously with the balance equations. This obtains the mole fractions of free $H_2S$ and $CO_2$ in solution. The equilibrium partial pressures of $H_2S$ and $CO_2$ are related to the respective free concentrations by Henry's constants:

$$\ln H_i = B_{1i} + B_{2i}/T$$

The apparent fugacities and partial molar enthalpies, Gibbs energies and entropies of $H_2S$ and $CO_2$ are calculated by standard thermodynamic relationships. The chemical reactions are always considered.

The values of the coefficients for the seven equilibrium constants ($A_{1i}$, ... $A_{5i}$) and for the two Henry's constants $B_{1i}$ and $B_{2i}$ are built into the Aspen Physical Property System. The coefficients for the equilibrium constants were determined by regression. All available data for the four amines were used: monoethanolamine, diethanolamine, disopropanolamine and diglycolamine.

You are not required to enter any parameters for this model.

### References

R.L. Kent and B. Eisenberg, Hydrocarbon Processing, (February 1976), pp. 87-92.

# Maxwell-Bonnell Vapor Pressure Model

The Maxwell-Bonnell model calculates vapor pressure using the Maxwell-Bonnell vapor pressure correlation for all hydrocarbon pseudo-components as a function of temperature. This is an empirical correlation based on API procedure 5A1.15, 5A1.13. This model is used in property method MXBONNEL for calculating vapor pressure and liquid fugacity coefficients (K-values).

### References

API procedure 5A1.15 and 5A1.13.

# Solid Antoine Vapor Pressure Model

The vapor pressure of a solid can be calculated using the Antoine equation.

Parameters for some components are available for the extended Antoine equation from the Aspen Physical Property System pure component databank. This equation can be used whenever the parameter PSANT is available.

The equation for the solid Antoine vapor pressure model is:

$$\ln p_i^{*,s} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} \quad \text{for } C_{4i} \leq T \leq C_{5i}$$

Extrapolation of $\ln p_i^{*,s}$ versus $1/T$ occurs outside of temperature bounds.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| PSANT/1 | $C_{1i}$ | — | x | — | — | PRESSURE, TEMPERATURE |
| PSANT/2 | $C_{2i}$ | — | x | — | — | TEMPERATURE |
| PSANT/3 | $C_{3i}$ | 0 | x | — | — | TEMPERATURE |
| PSANT/4 | $C_{4i}$ | 0 | x | — | — | TEMPERATURE |
| PSANT/5 | $C_{5i}$ | 1000 | x | — | — | TEMPERATURE |

# DIPPR/Watson/PPDS/IK-CAPE Heat of Vaporization Model

The Aspen Physical Property System has several submodels for calculating pure component heat of vaporization. It uses parameter THRSWT/4 to determine which submodel is used. See Pure Component Temperature-Dependent Properties for details.

| If THRSWT/4 is | Then this equation is used |
|---|---|
| 0 | Watson |
| 106 | DIPPR |
| 301 | PPDS |
| 401 | IK-CAPE |
| 505 | NIST TDE Watson equation |

## DIPPR Heat of Vaporization Equation

The DIPPR equation is used to calculate heat of vaporization when THRSWT/4 is set to 106. (Other DIPPR equations may sometimes be used. See Pure Component Temperature-Dependent Properties for details.)

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:

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

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

Linear extrapolation of $\Delta_{vap}H_i^*$ versus $T$ occurs outside of temperature bounds, using the slope at the temperature bound, except that $\Delta_{vap}H_i^*$ is zero for

$T \geq T_c$ .

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| DHVLDP/1 | $C_{1i}$ | — | x | — | — | MOLE-ENTHALPY |
| DHVLDP/2, ..., 5 | $C_{2i}$, ..., $C_{5i}$ | 0 | x | — | — | — |
| DHVLDP/6 | $C_{6i}$ | 0 | x | — | — | TEMPERATURE |
| DHVLDP/7 | $C_{7i}$ | 1000 | x | — | — | TEMPERATURE |
| TC | $T_{ci}$ | — | — | 5.0 | 2000.0 | TEMPERATURE |

# Watson Heat of Vaporization Equation

The Watson equation is used to calculate heat of vaporization when THRSWT/4 is set to 0. See Pure Component Temperature-Dependent Properties for details.

The equation for the Watson model is:

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

Where:

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

Linear extrapolation of $\Delta_{vap}H_i^*$ versus $T$ occurs below the minimum temperature bound, using the slope at the temperature bound.

| Parameter Name/Element | Symbol | Default | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|
| TC | $T_{ci}$ | — | 5.0 | 2000.0 | TEMPERATURE |
| DHVLWT/1 | $\Delta_{vap}H_i^*(T_1)$ | — | $5\times10^4$ | $5\times10^8$ | 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 |

# PPDS Heat of Vaporization Equation

The PPDS equation is used to calculate heat of vaporization when THRSWT/4 is set to 301. See Pure Component Temperature-Dependent Properties for details.

The equation for the PPDS model is:

$$\Delta_{vap}H_i^* = T_{ci}R\left(C_{1i}\tau^{1/3} + C_{2i}\tau^{2/3} + C_{3i}\tau + C_{4i}\tau^2 + C_{5i}\tau^6\right) \text{ for } C_{6i} \leq T \leq C_{7i}$$

$$\tau = 1 - T/T_{ci}$$

where $R$ is the gas constant.

2 **Thermodynamic Property Models**

Linear extrapolation of $\Delta_{vap}H_i^*$ versus $T$ occurs outside of temperature bounds, using the slope at the temperature bound.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TC | $T_{ci}$ | — | | 5.0 | 2000.0 | TEMPERATURE |
| DHVLDS/1 | $C_{1i}$ | — | — | — | — | — |
| DHVLDS/2 | $C_{2i}$ | 0 | — | — | — | — |
| DHVLDS/3 | $C_{3i}$ | 0 | — | — | — | — |
| DHVLDS/4 | $C_{4i}$ | 0 | — | — | — | — |
| DHVLDS/5 | $C_{5i}$ | 0 | — | — | — | — |
| DHVLDS/6 | $C_{6i}$ | 0 | | — | — | TEMPERATURE |
| DHVLDS/7 | $C_{7i}$ | 1000 | | — | — | TEMPERATURE |

# IK-CAPE Heat of Vaporization Equation

The IK-CAPE equation is used to calculate heat of vaporization when THRSWT/4 is set to 401. See Pure Component Temperature-Dependent Properties for details.

The equation for the IK-CAPE model is:

$$\Delta_{vap}H_i^*(T) = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

$$\text{for } C_{11i} \leq T \leq C_{12i}$$

Linear extrapolation of $\Delta_{vap}H_i^*$ versus $T$ occurs outside of temperature bounds, using the slope at the temperature bound

| 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 |

# NIST TDE Watson Heat of Vaporization Equation

The NIST TDE Watson equation is used to calculate heat of vaporization when THRSWT/4 is set to 505. See Pure Component Temperature-Dependent Properties for details.

The equation is:

$$\ln\left(\Delta_{vap}H_i^*\right) = C_{1i} + \sum_{m=2}^{nTerms} C_{mi}T_r^{m-2}\ln(1-T_r)$$

$$T_r = T/T_c$$

Linear extrapolation of $\Delta_{vap}H_i^*$ versus $T$ occurs outside of temperature bounds, using the slope at the temperature bound

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| DHVLTDEW/1 | $C_{1i}$ | — | X | — | — | — |
| DHVLTDEW/2, 3, 4 | $C_{2i}$, $C_{3i}$, $C_{4i}$ | 0 | X | — | — | — |
| DHVLTDEW/5 | $T_{ci}$ | — | X | — | — | TEMPERATURE |
| DHVLTDEW/6 | nTerms | 4 | X | — | — | — |
| DHVLTDEW/7 | $T_{lower}$ | 0 | X | — | — | TEMPERATURE |
| DHVLTDEW/8 | $T_{upper}$ | 1000 | X | — | — | TEMPERATURE |

# Clausius-Clapeyron Equation

The Aspen Physical Property System can calculate heat of vaporization using the Clausius Clapeyron equation:

$$\Delta_{vap}H_i^* = \frac{d\,p_i^{*,l}}{dT}\,T\left(V_i^{*,v} - V_i^{*,l}\right)$$

Where:

| | | |
|---|---|---|
| $\dfrac{d\,p_i^{*,l}}{dT}$ | = | Slope of the vapor pressure curve calculated from the Extended Antoine equation |
| $V_i^{*,v}$ | = | Vapor molar volume calculated from the Redlich Kwong equation of state |
| $V_i^{*,l}$ | = | Liquid molar volume calculated from the Rackett equation |

For parameter requirements, see Extended Antoine/Wagner, the Rackett model, and Redlich Kwong.

# Molar Volume and Density Models

The Aspen Physical Property System has nine built-in molar volume and density models available. This section describes the molar volume and density models.

| Model | Type |
|---|---|
| API Liquid Volume | Liquid volume |
| Brelvi-O'Connell | Partial molar liquid volume of gases |

| Model | Type |
|---|---|
| Clarke Aqueous Electrolyte Volume | Liquid volume |
| Costald Liquid Volume | Liquid volume |
| Debye-Hückel Volume | Electrolyte liquid volume |
| Liquid Constant Molar Volume Model | Liquid volume |
| Rackett/DIPPR/IK-CAPE Liquid Molar Volume | Liquid volume/liquid density |
| Rackett Mixture Liquid Volume | Liquid volume |
| Modified Rackett | Liquid volume |
| Aspen/IK-CAPE Solids Volume | Solid volume |
| Liquid Volume Quadratic Mixing Rule | Liquid volume |

# API Liquid Volume

This model calculates liquid molar volume for a mixture, using the API procedure and the Rackett model. Ideal mixing is assumed:

$$V_m^l = x_p V_p^l + x_r V_r^l$$

Where:

| | | |
|---|---|---|
| $x_p$ | = | Mole fraction of pseudocomponents |
| $x_r$ | = | Mole fraction of real components |

For pseudocomponents, the API procedure is used:

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

Where:

| | | |
|---|---|---|
| $fcn$ | = | A correlation based on API Figure 6A3.5 *(API Technical Data Book, Petroleum Refining, 4th edition)* |

At high density, the Ritter equation is used (adapted from Ritter, Lenoir, and Schweppe, *Petrol. Refiner* 37 [11] 225 (1958)):

$$V_p^l = \frac{1}{62.3636}\left[SG^2 - \frac{\left(1.2655SG - 0.5098 + 8.011\times10^{-5}T_b\right)\left(T - 519.67\right)}{T_b}\right]^{-1/2}$$

Where SG is the specific gravity, $T_b$ is the mean average boiling point in Rankine, $T$ is the temperature of the system in Rankine, and the mass volume is produced in units of cubic feet per pound-mass.

For real components, the mixture Rackett model is used:

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

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

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 | $Z^{RA}$ | ZC | — | 0.1 | 0.5 | — |

# Brelvi-O'Connell

The Brelvi-O'Connell model calculates partial molar volume of a supercritical component i at infinite dilution in pure solvent A. Partial molar volume at infinite dilution is required to compute the effect of pressure on Henry's constant. (See Henry's Constant.)

The general form of the Brelvi-O'Connell model is:

$$V_{iA}^{\infty} = fcn\left(V_i^{BO}, V_A^{BO}, V_A^{*l}\right)$$

Where:

| | | |
|---|---|---|
| *i* | = | Solute or dissolved-gas component |
| *A* | = | Solvent component |

The liquid molar volume of solvent is obtained from the Rackett model:

$$V_i^{*l} = \frac{RT_{cA}Z_A^{RA\left[1+(1-T_{rA})^{2/7}\right]}}{p_{cA}}$$

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

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

- Molar volume of molecular solvents (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.

If option code 1 is set to 1, the liquid volume quadratic mixing rule is used instead.

## Apparent Component Approach

For molecular solvents, the liquid molar volume is calculated by:

$$V_m^l = x_w V_w^* + x_{nws} V_{nws}^l \tag{1}$$

Where:

| | |
|---|---|
| $V_w^*$ | is calculated using the steam table. |
| $x_{nws}$ | is the sum of the mole fractions of all non-water solvents. |
| $V_{nws}^l$ | is the liquid molar volume for the mixture of all non-water solvents. It is calculated using the Rackett equation. |

For electrolytes:

$$V_{ca} = V_{ca}^\infty + A_{ca} \frac{\sqrt{x_{ca}}}{1 + \sqrt{x_{ca}}} \tag{2}$$

Where:

| | | |
|---|---|---|
| $x_{ca}$ | = | Apparent electrolyte mole fraction |

The mole fractions $x_{ca}$ are reconstituted arbitrarily from the true ionic concentrations, even if you use the apparent component approach. This technique is explained in Electrolyte Calculation in *Physical Property Methods*.

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:

| | | |
|---|---|---|
| $V_m^{l,t}$ | = | Liquid volume per number of true species |
| $V_m^{l,a}$ | = | Liquid volume per number of apparent species, $V_m^l$ of equation 1 |
| $n^a$ | = | Number of apparent species |
| $n^t$ | = | Number of true species |

The apparent molar volume is calculated as explained in the preceding subsection.

## Temperature Dependence

The temperature dependence of the molar volume of the solution is approximately equal to the temperature dependence of the molar volume of the solvent mixture:

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

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 $-0.12\times10^{-2}$ is used.

See also Rackett/Campbell-Thodos Mixture Liquid Volume for additional parameters used in the Rackett equation.

## Reference

C.C. Chen, private communication.

# COSTALD Liquid Volume

The equation for the COSTALD liquid volume model is:

$$V_m^{sat} = V_m^{CTD} V_m^{R,0} \left(1 - \omega V_m^{R,\delta}\right)$$

Where:

$V_m^{R,0}$ and $V_m^{R,\delta}$ are functions or $T_r$ for $0.25 < T_r \leq 0.95$

For $0.95 < T_r \leq 10$, 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 compressed liquid molar volume is calculated using the Tait equation:

$$V_m = V_m^{sat} \left(1 - C \ln\left(\frac{B + P}{B + P^{sat}}\right)\right)$$

Where $B$ and $C$ are functions of $T$, $\omega$, $T_c$, $P_c$ and $P^{sat}$ is the saturated pressure at $T$.

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

Mixing Rules:

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

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

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

Where:

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

To improve results, the Aspen Physical Property System uses a special correlation for water when this model is used. Changing the VSTCTD and OMGCTD parameters for water will not affect the results of the special correlation.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TC | $T_{ci}$ | — | — | 5.0 | 2000.0 | TEMPERATURE |
| VSTCTD | $V_r^{*,CTD}$ | VC | X | 0.001 | 3.5 | MOLE-VOLUME |
| OMGCTD | $\omega_r$ | 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.

# Debye-Hückel Volume

The Debye-Hückel model calculates liquid molar volume for aqueous electrolyte solutions.

The equation for the Debye-Hückel volume model is:

$$V_m = x_w V_w^{\bullet} + \sum_k x_k V_k$$

Where:

$V_k^{\infty}$ is the molar volume for water and is calculated from the ASME steam table.

$V_k$ is calculated from the Debye-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 $k$ |
| $A_V$ | = | Debye-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:

$$A_V = -2 \times 10^6 A_{\varphi} R \left( 3 \frac{\partial \ln \varepsilon_w}{\partial p} + \frac{1}{\rho_w} \frac{\partial \rho_w}{\partial p} \right)$$

Where:

| | | |
|---|---|---|
| $A_{\varphi}$ | = | Debye-Hückel constant for the osmotic coefficients (Pitzer, 1979) $\frac{1}{3} \left( 2\pi \left(10^{-3} \rho_w\right) N_A \right)^{1/2} \left( \frac{Q_e^2}{\varepsilon_w k_B T} \right)^{1/2}$ |
| $\rho_w$ | = | Density of water (kg / m$^3$) |
| $\varepsilon_w$ | = | Dielectric constant of water (Fm$^{-1}$), a function of pressure and temperature (Bradley and Pitzer, 1979) |

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

### References

D. J. Bradley, K. S. Pitzer, "Thermodynamics of Electrolytes," *J. Phys. Chem.*, 83 (12), 1599 (1979).

H.C. Helgeson and D.H. Kirkham, "Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressure and temperature. I. Thermodynamic/electrostatic properties of the solvent", *Am. J. Sci.*, 274, 1089 (1974).

K.S. Pitzer, "Theory: Ion Interaction Approach," *Activity Coefficients in Electrolyte Solutions,* Pytkowicz, R. ed., Vol. I, (CRC Press Inc., Boca Raton, Florida, 1979).

# Liquid Constant Molar Volume Model

This model, VL0CONS, uses a constant value entered by the user as the pure component liquid molar volume. It is not a function of temperature or pressure. This is used with the solids handling property method for modeling nonconventional solids.

| Parameter Name | Default | MDS | Units |
|---|---|---|---|
| VLCONS | 1 | x | MOLE-VOLUME |

# Rackett/DIPPR/PPDS/IK-CAPE Liquid Molar Volume

The Aspen Physical Property System has several submodels for calculating liquid molar volume. It uses parameter THRSWT/2 to determine which submodel is used. See Pure Component Temperature-Dependent Properties for details.

| If THRSWT/2 is | This equation is used | And this parameter is used |
|---|---|---|
| 0 | Rackett | RKTZRA |
| 100-116 | DIPPR | DNLDIP |
| 301 | PPDS | DNLPDS |
| 401 | IK-CAPE | VLPO |
| 503 | NIST ThermoML Polynomial | DNLTMLPO |
| 504 | NIST TDE expansion | DNLEXSAT |
| 514 | NIST TDE Rackett | DNLRACK |
| 515 | NIST COSTALD | DNLCOSTD |

For liquid molar volume of mixtures, the Rackett mixture equation is always used by default. This is not necessarily consistent with the pure component molar volume or density. If you need consistency, select route VLMX26 on the

**Properties | Property Methods** form. This route calculates mixture molar volume from the mole-fraction average of pure component molar volumes.

Many of these equations calculate density first, and return calculate liquid molar volume based on that density:

$$V_i^{*,l} = \frac{1}{\rho_i^{*,l}}$$

## DIPPR

DIPPR equation 105 is the default DIPPR equation for most substances:

$$\rho_i^{*,l} = C_{1i} / C_{2i}^{\left(1+(1-T/C_{3i})^{C_{4i}}\right)} \text{ for } C_{6i} \leq T \leq C_{7i}$$

This equation is similar to the Rackett equation.

DIPPR equation 116 is the default equation for water.

$$\rho_i^{*,l} = C_{1i} + C_{2i}\tau^{0.35} + C_{3i}\tau^{2/3} + C_{4i}\tau + C_{5i}\tau^{4/3} \text{ for } C_{6i} \leq T \leq C_{7i}$$

$$\tau = 1 - T / T_c$$

Other DIPPR equations, such as equation 100, may be used for some substances. Check the value of THRSWT/2 to determine the equation used. See Pure Component Temperature-Dependent Properties for details about DIPPR equations.

In either case, linear extrapolation of $\rho_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

| 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 |

† For equation 116, the units are MOLE-DENSITY for parameters DNLDIP/1 through DNLDIP/5 and the default for DNLDIP/3 is 0. For equation 105, DNLDIP/5 is not used, and absolute temperature units are assumed for DNLDIP/3.

## PPDS

The PPDS equation is:

$$\rho_i^{*,l} = \frac{1}{V_{ci}} + \frac{C_{1i}\tau^{0.35} + C_{2i}\tau^{2/3} + C_{3i}\tau + C_{4i}\tau^{4/3}}{M_i} \text{ for } C_{5i} \leq T \leq C_{6i}$$

$$\tau = \left(1 - T/T_c\right)$$

Linear extrapolation of $\rho_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

| 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 |
| TC | $T_{ci}$ | — | — | 5.0 | 2000.0 | TEMPERATURE |
| DNLPDS/1 | $C_{1i}$ | — | — | — | — | MASS-DENSITY |
| DNLPDS/2 | $C_{2i}$ | 0 | — | — | — | MASS-DENSITY |
| DNLPDS/3 | $C_{3i}$ | 0 | — | — | — | MASS-DENSITY |
| DNLPDS/4 | $C_{4i}$ | 0 | — | — | — | MASS-DENSITY |
| DNLPDS/5 | $C_{5i}$ | 0 | x | — | — | TEMPERATURE |
| DNLPDS/6 | $C_{6i}$ | 1000 | x | — | — | TEMPERATURE |

## 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 $C_{11i} \leq T \leq C_{12i}$

Linear extrapolation of $V_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

| 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 |

## NIST ThermoML Polynomial

This equation can be used when parameter DNLTMLPO is available.

$$\rho_i^{*,l} = \sum_{m=1}^{nTerms} C_{mi}T^{m-1}$$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| DNLTMLPO/1 | $C_{1i}$ | — | X | — | — | MOLE-DENSITY |
| DNLTMLPO/2, 3, 4 | $C_{2i}, C_{3i}, C_{4i}$ | 0 | X | — | — | MOLE-DENSITY TEMPERATURE |
| DNLTMLPO/5 | nTerms | 4 | X | — | — | — |
| DNLTMLPO/6 | $T_{lower}$ | 0 | X | — | — | TEMPERATURE |
| DNLTMLPO/7 | $T_{upper}$ | 1000 | X | — | — | TEMPERATURE |

# Rackett

The Rackett equation is:

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

Where:

$T_r = T \,/\, T_{ci}$

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

| 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 | — |

## NIST TDE Rackett Parameters

This equation can be used when the parameter DNLRACK is available.

$$V_i^{*,l} = \frac{RT_{ci}}{P_{ci} Z_{ci}^{-(1-T/T_n)^n}}$$

Linear extrapolation of $V_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| DNLRACK/1 | $Z_c$ | — | x | — | — | — |
| DNLRACK/2 | $n$ | 2/7 | x | — | — | — |
| DNLRACK/3 | $T_{ci}$ | — | x | — | — | TEMPERATURE |
| DNLRACK/4 | $p_{ci}$ | 0 | x | — | — | PRESSURE |
| DNLRACK/5 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| DNLRACK/6 | $T_{upper}$ | 1000 | x | — | — | TEMPERATURE |

## NIST COSTALD Parameters

This equation can be used when the parameter DNLCOSTD is available.

$$T_r = T/T_{ci}$$

$$\tau = 1 - T_r$$

$$v_0 = 1 - 1.52816\tau^{1/3} + 1.43907\tau^{2/3} - 0.81446\tau + 0.190454\tau^{4/3}$$

$$v_\delta = \frac{-0.296123 + 0.386914T_r - 0.0427258T_r^2 - 0.0480645T_r^3}{T_r - 1.00001}$$

$$\rho_i^{*,l} = \frac{0.001}{V_{oi}v_0(1 - \Omega v_\delta)}$$

Linear extrapolation of $V_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| DNLCOSTD/1 | $V_{oi}$ | — | x | — | — | VOLUME |
| DNLCOSTD/2 | $\Omega$ | 0 | x | — | — | — |
| DNLCOSTD/3 | $T_{ci}$ | — | x | — | — | TEMPERATURE |
| DNLCOSTD/4 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| DNLCOSTD/5 | $T_{upper}$ | 1000 | x | — | — | TEMPERATURE |

### NIST TDE Expansion

This equation can be used when the parameter DNLEXSAT is available.

$$\rho_i^{*,l} = \rho_{ci} + C_{1i}\tau^{0.35} + \sum_{m=2}^{nTerms} C_{mi}\tau^{m-1}$$

$$\tau = 1 - T/T_{ci}$$

Linear extrapolation of $V_i^{*,l}$ versus $T$ occurs outside of temperature bounds.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| DNLEXSAT/1 | $\rho_{ci}$ | — | x | — | — | MOLE-DENSITY |
| DNLEXSAT/2 | $C_{1i}$ | — | x | — | — | MOLE-DENSITY |
| DNLEXSAT/3, ..., DNLEXSAT/7 | $C_{2i}, ..., C_{6i}$ | 0 | x | — | — | MOLE-DENSITY |
| DNLEXSAT/8 | $T_{ci}$ | — | x | — | — | TEMPERATURE |
| DNLEXSAT/9 | $nTerms$ | 6 | x | — | — | — |
| DNLEXSAT/10 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| DNLEXSAT/11 | $T_{upper}$ | 1000 | x | — | — | TEMPERATURE |

### References

H.G. Rackett, *J.Chem. Eng. Data.*, Vol. 15, (1970), p. 514.

C.F. Spencer and R.P. Danner, *J. Chem. Eng. Data*, Vol. 17, (1972), p. 236.

# Rackett/Campbell-Thodos Mixture Liquid Volume

The Rackett equation calculates liquid molar volume for all activity coefficient based and petroleum tuned equation of state based property methods. In the last category of property methods, the equation is used in conjunction with the API model. The API model is used for pseudocomponents, while the Rackett model is used for real components. (See API Liquid Volume .) Campbell-Thodos is a variation on the Rackett model which allows the compressibility term $Z_i^{*,RA}$ to vary with temperature.

## Rackett

The equation for the Rackett model is:

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

Where:

| | | |
|---|---|---|
| $T_c$ | = | $\sum_i \sum_j x_i x_j V_{ci} V_{cj} \left( T_{ci} T_{cj} \right)^{1/2} \left( 1 - k_{ij} \right) / V_{cm}^2$ |
| $\dfrac{T_c}{P_c}$ | = | $\sum_i x_i \dfrac{T_{ci}}{P_{ci}}$ |
| $Z_m^{RA}$ | = | $\sum_i x_i Z_i^{*,RA}$ |
| $V_{cm}$ | = | $\sum_i x_i V_{ci}$ |
| $T_r$ | = | $T / T_c$ |

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TC | $T_{ci}$ | — | — | 5.0 | 2000.0 | TEMPERATURE |
| PC | $p_{ci}$ | — | — | $10^5$ | $10^8$ | PRESSURE |
| VCRKT | $V_{ci}$ | VC | x | 0.001 | 3.5 | MOLE-VOLUME |
| RKTZRA | $Z_i^{*,RA}$ | ZC | x | 0.1 | 1.0 | — |
| RKTKIJ | $k_{ij}$ | $1 - \dfrac{8 \left( V_{ci} V_{cj} \right)^{1/2}}{\left( V_{ci}^{1/3} + V_{cj}^{1/3} \right)^3}$ | x | -5.0 | 5.0 | — |

## Campbell-Thodos

The Campbell-Thodos model uses the same equation and parameters as the Rackett model, above, except that $Z_m^{RA}$ is allowed to vary with temperature:

$$Z_m^{RA} = \sum_i x_i Z_i^{*,RA}[1 + d_i(1 - T_r)]$$

Campbell-Thodos also uses separately-adjustable versions of the critical parameters. Tmin and Tmax define the temperature range where the equation is applicable.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| RACKET/1 | $R*T_{ci}/P_{ci}$ | R*Tci/Pci | — | — | — | MOLE-VOLUME |
| RACKET/2 | $Z_i^{*,RA}$ | RKTZRA | x | 0.1 | 1.0 | — |
| RACKET/3 | $d_i$ | 0 | x | 0 | 0.11 | — |
| RACKET/4 | $T_{min}$ | 0 | x | — | — | TEMPERATURE |
| RACKET/5 | $T_{max}$ | 1000 | x | — | — | TEMPERATURE |

The Campbell-Thodos model is used when RACKET/3 is set to a value less than 0.11. The default value, 2/7, indicates that the standard Rackett equation should be used. When Campbell-Thodos is not used, RACKET/3 should be kept at its default value of 2/7 for all components.

## References

H.G. Rackett, *J.Chem, Eng. Data.*, Vol. 15, (1970), p. 514.

C.F. Spencer and R.P. Danner, *J. Chem. Eng. Data*, Vol. 17, (1972), p. 236.

# Modified Rackett Liquid Molar Volume

The Modified Rackett equation improves the accuracy of liquid mixture molar volume calculation by introducing additional parameters to compute the pure component parameter RKTZRA and the binary parameter $k_{ij}$.

The equation for the Modified Rackett model is:

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

Where:

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

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

| | | |
|---|---|---|
| $\dfrac{T_c}{P_c}$ | $=$ | $\sum_i x_i \dfrac{T_{ci}}{P_{ci}}$ |
| $Z_m^{RA}$ | $=$ | $\sum_i x_i Z_i^{*,RA}$ |
| $Z_i^{*,RA}$ | $=$ | $a_i + b_i T + c_i T^2$ |
| $V_{cm}$ | $=$ | $\sum_i x_i V_{ci}$ |
| $T_r$ | $=$ | $T / T_c$ |

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| MRKZRA/1 | $a_i$ | RKTZRA | x | 0.1 | 0.5 | — |
| MRKZRA/2 | $b_i$ | 0 | x | — | — | — |
| MRKZRA/3 | $c_i$ | 0 | x | — | — | — |
| MRKKIJ/1 | $A_{ij}$ | $1 - \dfrac{8\left(V_{ci}V_{cj}\right)^{1/2}}{\left(V_{ci}^{1/3} + V_{cj}^{1/3}\right)^{3}}$ | x | — | — | — |
| MRKKIJ/2 | $B_{ij}$ | 0 | x | — | — | — |
| MRKKIJ/3 | $C_{ij}$ | 0 | x | — | — | — |

### References

H.G. Rackett, *J.Chem, Eng. Data.*, Vol. 15, (1970), p. 514.

C.F. Spencer and R.P. Danner, *J. Chem. Eng. Data*, Vol. 17, (1972), p. 236.

# Aspen/DIPPR/IK-CAPE Solid Molar Volume

The Aspen Physical Property System has several submodels for calculating solid molar volume. It uses parameter THRSWT/1 to determine which submodel is used. See Pure Component Temperature-Dependent Properties for details.

| If THRSWT/1 is | This equation is used | And this parameter is used |
|---|---|---|
| 0 | Aspen | VSPOLY |
| 100 | DIPPR | DNSDIP |
| 401 | IK-CAPE | VSPO |
| 503 | NIST ThermoML polynomial | DNSTMLPO |

## Aspen Polynomial

The equation for the Aspen solids volume polynomial is:

$$V_i^{*,s} = C_{1i} + C_2 T + C_{3i} T^2 + C_{4i} T^3 + C_{5i} T^4 \text{ for } C_{6i} \le T \le C_{7i}$$

Linear extrapolation of $V_i^{*,s}$ versus $T$ occurs outside of temperature bounds.

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

## IK-CAPE Equation

The IK-CAPE equation is:

$$V_i^{*,s} = C_{1i} + C_{2i} T + C_{3i} T^2 + C_{4i} T^3 + C_{5i} T^4 + C_{6i} T^5 + C_{7i} T^6 + C_{8i} T^7 + C_{9i} T^8 + C_{10i} T^9$$

$$\text{for } C_{11i} \le T \le C_{12i}$$

Linear extrapolation of $V_i^{*,s}$ versus $T$ occurs outside of temperature bounds.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| VSPO/1 | $C_{1i}$ | — | X | — | — | MOLE-VOLUME |
| VSPO/2, ..., 10 | $C_{2i}$, ..., $C_{10i}$ | 0 | X | — | — | MOLE-VOLUME TEMPERATURE |
| VSPO/11 | $C_{11i}$ | 0 | X | — | — | TEMPERATURE |
| VSPO/12 | $C_{12i}$ | 1000 | X | — | — | TEMPERATURE |

## DIPPR

The DIPPR equation is:

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

Linear extrapolation of $\rho_i^{*,s}$ versus $T$ occurs outside of temperature bounds.

$$V_i^{*,s} = 1 / \rho_i^{*,s}$$

(Other DIPPR equations may sometimes be used. See Pure Component Temperature-Dependent Properties for details.)

The model returns solid molar volume for pure components.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| DNSDIP/1 | $C_{1i}$ | — | x | — | — | MOLE- |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| | | | | | | DENSITY |
| DNSDIP/2, ..., 5 | $C_{2i}$, ..., $C_{5i}$ | 0 | x | — | — | MOLE-DENSITY, TEMPERATURE |
| DNSDIP/6 | $C_{6i}$ | 0 | x | — | — | TEMPERATURE |
| DNSDIP/7 | $C_{7i}$ | 1000 | x | — | — | TEMPERATURE |

### NIST ThermoML Polynomial

$$\rho_i^{*,s} = \sum_{m=1}^{nTerms} C_{mi} T^{m-1}$$

Linear extrapolation of $\rho_i^{*,s}$ versus $T$ occurs outside of temperature bounds.

$V_i^{*,s} = 1 / \rho_i^{*,s}$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| DNSTMLPO/1 | $C_{1i}$ | — | x | — | — | MOLE-DENSITY |
| DNSTMLPO/2,...,8 | $C_{2i}$, ..., $C_{8i}$ | 0 | x | — | — | MOLE-DENSITY, TEMPERATURE |
| DNSTMLPO/9 | $nTerms$ | 8 | x | — | — | — |
| DNSTMLPO/10 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| DNSTMLPO/11 | $T_{upper}$ | 1000 | x | — | — | TEMPERATURE |

# Liquid Volume Quadratic Mixing Rule

With $i$ and $j$ being components, the liquid volume quadratic mixing rule is:

$$V_m^l = \sum_i x_i V_i^{*,l} + \sum_i x_i \sum_j x_j K_{ij} \left( V_i^{*,l} V_j^{*,l} \right)^{0.5}$$

### Option Codes

| Option Code | Value | Descriptions |
|---|---|---|
| 1 | 0 | Use normal pure component liquid volume model for all components (default) |
| | 1 | Use steam tables for water |
| 2 | 0 | Use mole basis composition (default) |
| | 1 | Use mass basis composition |

### Parameter

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| VLQKIJ | $K_{ij}$ | - | x | - | - | — |

# Heat Capacity Models

The Aspen Physical Property System has five built-in heat capacity models. This section describes the heat capacity models available.

| Model | Type |
|---|---|
| Aqueous Infinite Dilution Heat Capacity Polynomial | Electrolyte liquid |
| Criss-Cobble Aqueous Infinite Dilution Ionic Heat Capacity | Electrolyte liquid |
| DIPPR/IK-CAPE Liquid Heat Capacity | Liquid |
| Aspen/DIPPR/Barin/IK-CAPE Ideal Gas Heat Capacity | Ideal gas |
| Aspen/DIPPR/Barin/IK-CAPE Solid Heat Capacity | 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:

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

$C_{p,i}^{\infty,aq}$ versus $T$ is linearly extrapolated using the slope at $C_{7i}$ for $T < C_{7i}$

$C_{p,i}^{\infty,aq}$ versus $T$ is linearly extrapolated using the slope at $C_{8i}$ for $T < C_{8i}$

| Parameter Name/Element | Applicable Components | Symbol | Default | Units |
|---|---|---|---|---|
| CPAQ0/1 | Ions, molecular solutes | $C_{1i}$ | — | TEMPERATURE and HEAT CAPACITY |
| CPAQ0/2,…,6 | Ions, molecular solutes | $C_{2i}, ..., C_{6i}$ | 0 | TEMPERATURE and HEAT CAPACITY |
| CPAQ0/7 | Ions, molecular solutes | $C_{7i}$ | 0 | TEMPERATURE |
| CPAQ0/8 | Ions, molecular solutes | $C_{8i}$ | 1000 | TEMPERATURE |

If any of $C_{4i}$ through $C_{6i}$ is non-zero, absolute temperature units are assumed for $C_{1i}$ through $C_{6i}$. Otherwise, user input units for temperature are used. The temperature limits are always interpreted in user input units.

# 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 | $S_a^{\infty,aq}$ | $\dfrac{\Delta_f H_a^{\infty,aq}(T-298) - \Delta_f G_a^{\infty,aq}(T=298)}{29815}$ | MOLE-ENTROPY |
| | Cations | $S_a^{\infty,aq}$ | $\dfrac{\Delta_f H_a^{\infty,aq}(T-298) - \Delta_f G_a^{\infty,aq}(T=298)}{29815}$ | MOLE-ENTROPY |

# DIPPR/PPDS/IK-CAPE Liquid Heat Capacity

The Aspen Physical Property System has several submodels for calculating liquid heat capacity. It uses parameter THRSWT/6 to determine which submodel is used. See Pure Component Temperature-Dependent Properties for details.

| If THRSWT/6 is | This equation is used | And this parameter is used |
|---|---|---|
| 100 | DIPPR | CPLDIP |
| 200 | Barin | CPLXP1, CPLXP2 |
| 301 | PPDS | CPLPDS |
| 401 | IK-CAPE heat capacity polynomial | CPLPO |
| 403 | IK-CAPE liquid heat capacity | CPLIKC |
| 503 | NIST ThermoML polynomial | CPLTMLPO |
| 506 | NIST TDE equation | CPLTDECS |

The DIPPR/PPDS/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:

- One of the parameters for calculating heat capacity (see table below) is available.
- The component is not supercritical (HENRY-COMP).

The model uses a specific method (see Methods in Property Calculation Methods and Routes):

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

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

Where

| | | |
|---|---|---|
| $H_i^{*,l}(T^{ref})$ | = | Reference enthalpy calculated at $T^{ref}$ |
| $H_i^{*,ig}$ | = | Ideal gas enthalpy |
| $H_i^{*,v} - H_i^{*,ig}$ | = | Vapor enthalpy departure |
| $\Delta_{vap} H_i^{*,l}$ | = | Enthalpy of vaporization |

$T^{ref}$ 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 model 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.

## DIPPR Liquid Heat Capacity

The DIPPR equation is used to calculate liquid heat capacity when parameter THRSWT/6 is 100.

The DIPPR equation is:

$$C_{p,i}^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 \quad for \ C_{6i} \leq T \leq C_{7i}$$

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 | $C_{1i}$ | — | x | — | — | MOLE-HEAT-CAPACITY, TEMPERATURE |
| CPLDIP/2, ..., 5 | $C_{2i}$, ..., $C_{5i}$ | 0 | x | — | — | MOLE-HEAT-CAPACITY, TEMPERATURE |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPLDIP/6 | $C_{6i}$ | 0 | x | — | — | TEMPERATURE |
| CPLDIP/7 | $C_{7i}$ | 1000 | x | — | — | TEMPERATURE |
| TREFHL | $T^{ref}$ | 298.15 | — | — | — | TEMPERATURE |
| COMPHL | — | — | — | — | — | — |

To specify that the model is used for a component, enter a value of 1.0 for COMPHL.

(Other DIPPR equations may sometimes be used. See Pure Component Temperature-Dependent Properties for details.)


# PPDS Liquid Heat Capacity

The PPDS equation is used to calculate liquid heat capacity when parameter THRSWT/6 is 301.

The PPDS equation is:

$$C_p^{*,l} = R\left(C_{1i}/\tau + C_{2i} + C_{3i}\tau + C_{4i}\tau^2 + C_{5i}\tau^3 + C_{6i}\tau^4\right)$$

$$\text{for } C_{7i} \leq T \leq C_{8i} \text{ and } T \leq 0.9 T_c$$

$$\tau = 1 - T/T_c$$

Where $R$ is the gas constant.

Linear extrapolation occurs for $C_p^{*,l}$ versus T outside of bounds.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPLPDS/1 | $C_{1i}$ | — | — | — | — | — |
| CPLPDS/2 | $C_{2i}$ | 0 | — | — | — | — |
| CPLPDS/3 | $C_{3i}$ | 0 | — | — | — | — |
| CPLPDS/4 | $C_{4i}$ | 0 | — | — | — | — |
| CPLPDS/5 | $C_{5i}$ | 0 | — | — | — | — |
| CPLPDS/6 | $C_{6i}$ | 0 | — | — | — | — |
| CPLPDS/7 | $C_{7i}$ | 0 | x | — | — | TEMPERATURE |
| CPLPDS/8 | $C_{8i}$ | 1000 | x | — | — | TEMPERATURE |


# IK-CAPE Liquid Heat Capacity

Two IK-CAPE equations can be used to calculate liquid heat capacity. Linear extrapolation occurs for $C_p^{*,l}$ versus $T$ outside of bounds for either equation.

When THRSWT/6 is 403, the IK-CAPE liquid heat capacity equation is used. The equation is:

$$C_{p,i}^{*,l} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + \frac{C_{5i}}{T^2} \quad for\, C_{6i} \leq T \leq C_{7i}$$

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

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPLIKC/1 | $C_{1i}$ | — T | x | — | — | MOLE-HEAT-CAPACITY |
| CPLIKC/2,...,4 | $C_{2i}$, ..., $C_{4i}$ | 0 | x | — | — | MOLE-HEAT-CAPACITY, TEMPERATURE |
| CPLIKC/5 | $C_{5i}$ | 0 | x | — | — | MOLE-HEAT-CAPACITY, TEMPERATURE † |
| CPLIKC/6 | $C_{6i}$ | 0 | x | — | — | TEMPERATURE |
| CPLIKC/7 | $C_{7i}$ | 1000 | x | — | — | TEMPERATURE |

† If $C_{5i}$ is non-zero, absolute temperature units are assumed for $C_{2i}$ through $C_{5i}$. Otherwise, user input units for temperature are used. The temperature limits are always interpreted in user input units.

When THRSWT/6 is 401, the IK-CAPE heat capacity polynomial is used.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 |
|---|---|---|---|---|---|---|
| CPLPO/1 | $C_{1i}$ | — | X | — | — | MOLE-CAPACITY |
| CPLPO/2,…,10 | $C_{2i}$, ..., $C_{10i}$ | 0 | X | — | — | MOLE-CAPACITY TEMPERATURE |
| CPLPO/11 | $C_{11i}$ | 0 | X | — | — | TEMPERATURE |
| CPLPO/12 | $C_{12i}$ | 1000 | X | — | — | TEMPERATURE |

See Pure Component Temperature-Dependent Properties for details on the THRSWT parameters.

## NIST Liquid Heat Capacity

Two NIST equations can be used to calculate liquid heat capacity. Linear extrapolation occurs for $C_p^{*,l}$ versus $T$ outside of bounds for either equation.

When THRSWT/6 is 503, the ThermoML polynomial is used to calculate liquid heat capacity:

$$C_{p,i}^{*,l} = \sum_{m=1}^{nTerms} C_{mi}T^{m-1}$$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPLTMLPO/1 | $C_{1i}$ | — | X | — | — | J/K^2/mol |
| CPLTMLPO/2,…,5 | $C_{2i}$, ..., $C_{5i}$ | 0 | X | — | — | J/K^2/mol |
| CPLTMLPO/6 | nTerms | 5 | X | — | — | — |
| CPLTMLPO/7 | $T_{lower}$ | 0 | X | — | — | TEMPERATURE |

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPLTMLPO/8 | $T_{upper}$ | 1000 | X | — | — | TEMPERATURE |

When THRSWT/6 is 506, the TDE equation is used to calculate liquid heat capacity:

$$C_{p,i}^{*,l} = B/\tau + \sum_{m=1}^{nTerms} C_{mi}\tau^{m-1}$$

$$\tau = 1 - T/T_{ci}$$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPLTDECS/1 | $C_{1i}$ | — | X | — | — | MOLE-HEAT-CAPACITY |
| CPLTDECS/2,…,4 | $C_{2i}$, …, $C_{4i}$ | 0 | X | — | — | MOLE-HEAT-CAPACITY |
| CPLTDECS/5 | $B$ | 0 | X | — | — | MOLE-HEAT-CAPACITY |
| CPLTDECS/6 | $T_{ci}$ | — | X | — | — | TEMPERATURE |
| CPLTDECS/7 | nTerms | 4 | X | — | — | — |
| CPLTDECS/8 | $T_{lower}$ | 0 | X | — | — | TEMPERATURE |
| CPLTDECS/9 | $T_{upper}$ | 1000 | X | — | — | TEMPERATURE |

See Pure Component Temperature-Dependent Properties for details on the THRSWT parameters.

# Aspen/DIPPR/Barin/PPDS/IK-CAPE Ideal Gas Heat Capacity

The Aspen Physical Property System has several submodels for calculating ideal gas heat capacity. It uses parameter THRSWT/7 to determine which submodel is used. See Pure Component Temperature-Dependent Properties for details.

| If THRSWT/7 is | This equation is used | And this parameter is used |
|---|---|---|
| 0 | Ideal gas heat capacity polynomial | CPIG |
| 107 | DIPPR | CPIGDP |
| 200 | Barin | CPIXP1, CPIXP2, CPIXP3 |
| 301 | PPDS | CPIGDS |
| 401 | IK-CAPE heat capacity polynomial | CPIGPO |
| 503 | NIST ThermoML polynomial | CPITMLPO |
| 513 | NIST Aly-Lee | CPIALEE |

These equations are also used to calculate ideal gas enthalpies, entropies, and Gibbs energies.

## Aspen Ideal Gas Heat Capacity Polynomial

The ideal gas heat capacity polynomial is available for components stored in ASPENPCD, AQUEOUS, and SOLIDS databanks. This model is also used in PCES.

$$C_p^{*,ig} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 \text{ for } C_{7i} \leq T \leq C_{8i}$$

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

$C_p^{*,ig}$ is linearly extrapolated using slope at $C_{8i}$ for $T > C_{8i}$

| 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 $C_{10i}$ or $C_{11i}$ is non-zero, then absolute temperature units are assumed for $C_{9i}$ through $C_{11i}$. Otherwise, user input temperature units are used for all parameters. User input temperature units are always used for $C_{1i}$ through $C_{8i}$.

## NIST ThermoML Polynomial

This equation can be used when parameter CPITMLPO is available.

$$C_p^{*,ig} = \sum_{m=1}^{nTerms} C_{mi}T^{m-1}$$

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPITMLPO /1 | $C_{1i}$ | — | x | — | — | J/K^2/mol |
| CPITMLPO /2, ..., 6 | $C_{2i}, ..., C_{6i}$ | 0 | x | — | — | J/K^2/mol |
| CPITMLPO/7 | nTerms | 6 | x | — | — | — |
| CPITMLPO /8 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| CPITMLPO /9 | $T_{upper}$ | 1000 | x | — | — | TEMPERATURE |

## DIPPR

The DIPPR ideal gas heat capacity equation by Aly and Lee 1981 is:

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

No extrapolation is used with this equation.

(Other DIPPR equations may sometimes be used. See Pure Component Temperature-Dependent Properties for details.)

| 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 |

†† Absolute temperature units are assumed for $C_{3i}$ and $C_{5i}$. The temperature limits are always interpreted in user input units.

## NIST Aly-Lee

This equation is the same as the DIPPR Aly and Lee equation above, but it uses a different parameter set. Note that elements 6 and 7 of the CPIALEE parameter are not used in the equation.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPIALEE/1 | $C_{1i}$ | — | x | — | — | MOLE-HEAT-CAPACITY |
| CPIALEE/2 | $C_{2i}$ | 0 | x | — | — | MOLE-HEAT-CAPACITY |
| CPIALEE/3 | $C_{3i}$ | 0 | x | — | — | TEMPERATURE †† |
| CPIALEE/4 | $C_{4i}$ | 0 | x | — | — | MOLE-HEAT-CAPACITY |
| CPIALEE/5 | $C_{5i}$ | 0 | x | — | — | TEMPERATURE †† |
| CPIALEE/8 | $C_{6i}$ | 0 | x | — | — | TEMPERATURE |
| CPIALEE/9 | $C_{7i}$ | 1000 | x | — | — | TEMPERATURE |

†† Absolute temperature units are assumed for $C_{3i}$ and $C_{5i}$. The temperature limits are always interpreted in user input units.

## PPDS

The PPDS equation is:

$$C_p^{*,ig} = R\left[C_{2i} + \left(C_{3i} - C_{2i}\right)y^2\left(1 + (y-1)\left(C_{4i} + C_{5i}y + C_{6i}y^2 + C_{7i}y^3 + C_{8i}y^4\right)\right)\right]$$

$$y = \frac{T}{T + C_{1i}}$$

for $C_{9i} \leq T \leq C_{10i}$

where $R$ is the gas constant.

2 **Thermodynamic Property Models**

Linear extrapolation of $C_p^{*,ig}$ versus $T$ is performed outside temperature bounds.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPIGDS/1 | $C_{1i}$ | — | — | — | — | TEMPERATURE |
| CPIGDS/2, …, 8 | $C_{2i}$, …, $C_{8i}$ | 0 | — | — | — | — |
| CPIGDS/9 | $C_{9i}$ | 0 | — | — | — | TEMPERATURE |
| CPIGDS/10 | $C_{10i}$ | 1000 | — | — | — | TEMPERATURE |

## IK-CAPE Heat Capacity Polynomial

The equation is:

$$C_p^{\bullet} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

$$\text{for} \quad C_{11i} \leq T \leq C_{12i}$$

Linear extrapolation of $C_p^{*,ig}$ versus $T$ is performed outside temperature bounds.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPIGPO/1 | $C_{1i}$ | — | X | — | — | MOLE-CAPACITY |
| CPIGPO/2,…,10 | $C_{2i}$, …, $C_{10i}$ | 0 | X | — | — | MOLE-CAPACITY TEMPERATURE |
| CPIGPO/11 | $C_{11i}$ | 0 | X | — | — | TEMPERATURE |
| CPIGPO/12 | $C_{12i}$ | 1000 | X | — | — | TEMPERATURE |

## References

Data for the Ideal Gas Heat Capacity Polynomial: Reid, Prausnitz and Poling, The Properties of Gases and Liquids, 4th ed., (New York: McGraw-Hill, 1987).

The Aspen Physical Property System combustion data bank, JANAF Thermochemical Data, Compiled and calculated by the Thermal Research Laboratory of Dow Chemical Company.

F. A. Aly and L. L. Lee, "Self-Consistent Equations for Calculating the Ideal Gas Heat Capacity, Enthalpy, and Entropy, Fluid Phase Eq., Vol. 6, (1981), p. 169.

# Aspen/DIPPR/Barin/IK-CAPE Solid Heat Capacity

The Aspen Physical Property System has several submodels for calculating solid heat capacity. It uses parameter THRSWT/5 to determine which submodel is used. See Pure Component Temperature-Dependent Properties for details.

| If THRSWT/5 is | This equation is used | And this parameter is used |
|---|---|---|
| 0 | Aspen solid heat capacity polynomial | CPSPO1 |
| 100 | DIPPR | CPSDIP |
| 200 | Barin | CPSXP1, CPSXP2, …, CPSXP7 |
| 401 | IK-CAPE heat capacity polynomial | CPSPO |
| 503 | NIST ThermoML polynomial | CPSTMLPO |

The enthalpy, entropy, and Gibbs energy of solids are also calculated from these equations:

## Aspen Solid Heat Capacity Polynomial

The Aspen equation is:

$$C_{p,i}^{*,s} = C_{1i} + C_{2i}T + C_{3i}T^2 + \frac{C_{4i}}{T} + \frac{C_{5i}}{T^2} + \frac{C_{6i}}{\sqrt{T}} \text{ for } C_{7i} \leq T \leq C_{8i}$$

Linear extrapolation occurs for $C_{p,i}^{*,s}$ versus T outside of bounds.

| Parameter Name | Applicable Components | Symbol | MDS | Default | Units |
|---|---|---|---|---|---|
| CPSPO1/1 | Solids, Salts | $C_{1i}$ | x | — | † |
| CPSPO1/2, …, 6 | Solids, Salts | $C_{2i}$, …, $C_{6i}$ | x | 0 | † |
| CPSPO1/7 | Solids, Salts | $C_{7i}$ | x | 0 | † |
| CPSPO1/8 | Solids, Salts | $C_{8i}$ | x | 1000 | † |

† The units are TEMPERATURE and HEAT-CAPACITY for all elements. If any of $C_{4i}$ through $C_{6i}$ are non-zero, absolute temperature units are assumed for elements $C_{1i}$ through $C_{6i}$. Otherwise, user input temperature units are assumed for all elements. The temperature limits are always interpreted in user input units.

## DIPPR

The DIPPR equation is:

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

Linear extrapolation occurs for $C_{p,i}^{*,s}$ versus T outside of bounds.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPSDIP/1 | $C_{1i}$ | — | x | — | — | MOLE-HEAT-CAPACITY, TEMPERATURE |
| CPSDIP/2,…,5 | $C_{2i}$, …, $C_{5i}$ | 0 | x | — | — | MOLE-HEAT-CAPACITY, TEMPERATURE |
| CPSDIP/6 | $C_{6i}$ | 0 | x | — | — | TEMPERATURE |
| CPSDIP/7 | $C_{7i}$ | 1000 | x | — | — | TEMPERATURE |

(Other DIPPR equations may sometimes be used. See Pure Component Temperature-Dependent Properties for details.)

## NIST ThermoML Polynomial

The equation is:

$$C_{p,i}^{*,s} = \sum_{m=1}^{nTerms} C_{mi} T^{m-1}$$

Linear extrapolation occurs for $C_{p,i}^{*,s}$ versus T outside of bounds.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPSTMLPO/1 | $C_{1i}$ | — | x | — | — | J/K^2/mol |
| CPSTMLPO/2,…,5 | $C_{2i}, …, C_{5i}$ | 0 | x | — | — | J/K^2/mol |
| CPSTMLPO/6 | nTerms | 5 | x | — | — | — |
| CPSTMLPO/7 | $T_{lower}$ | 0 | x | — | — | TEMPERATURE |
| CPSTMLPO/8 | $T_{upper}$ | 1000 | x | — | — | TEMPERATURE |

## IK-CAPE Heat Capacity Polynomial

The equation is:

$$C_p^* = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5 + C_{7i}T^6 + C_{8i}T^7 + C_{9i}T^8 + C_{10i}T^9$$

$$\text{for} \quad C_{11i} \leq T \leq C_{12i}$$

Linear extrapolation occurs for $C_{p,i}^{*,s}$ versus T outside of bounds.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPSPO/1 | $C_{1i}$ | — | X | — | — | MOLE-CAPACITY |
| CPSPO/2,…,10 | $C_{10i}$ | 0 | X | — | — | MOLE-CAPACITY TEMPERATURE |
| CPSPO/11 | $C_{11i}$ | 0 | X | — | — | TEMPERATURE |
| CPSPO/12 | $C_{12i}$ | 1000 | X | — | — | TEMPERATURE |

# Solubility Correlations

The Aspen Physical Property System has three 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 |
| Hydrocarbon solubility | Hydrocarbon solubility in water-rich 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:

| | | |
|---|---|---|
| $w_A$ | = | $\dfrac{x_A\left(V_{cA}\right)^{\frac{2}{3}}}{\sum_B x_B\left(V_{cB}\right)^{\frac{2}{3}}}$ |
| $\ln H_{iA}(T, p_A^{*,l})$ | = | $a_{iA} + b_{iA}/T + c_{iA}\ln T + d_{iA}T + e_{iA}/T^2 \ \ \text{for}\ T_L \leq T \leq T_H$ |

Linear extrapolation occurs for ln $H_{iA}$ versus $T$ outside of bounds.

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

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 $a_{iA}$, $b_{iA}$, $c_{iA}$, $d_{iA}$, and $e_{iA}$ are specific to a solute-solvent pair. They can be obtained from regression of gas solubility data. The Aspen Physical Property System has a large number of built-in Henry's constants for many solutes in solvents. These parameters were obtained using data from the Dortmund Databank. See Physical Property Data, Chapter 1, for details.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| VC | $V_{cA}$ | — | — | 0.001 | 3.5 | MOLE-VOLUME |
| HENRY/1 | $a_{iA}$ | †† | x | — | — | PRESSURE, TEMPERATURE † |
| HENRY/2 | $b_{iA}$ | 0 | x | — | — | TEMPERATURE † |
| HENRY/3 | $c_{iA}$ | 0 | x | — | — | TEMPERATURE † |
| HENRY/4 | $d_{iA}$ | 0 | x | — | — | TEMPERATURE † |
| HENRY/5 | $T_L$ | 0 | x | — | — | TEMPERATURE |
| HENRY/6 | $T_H$ | 2000 | x | — | — | TEMPERATURE |
| HENRY/7 | $e_{iA}$ | 0 | x | — | — | TEMPERATURE † |

† If any of $b_{iA}$, $c_{iA}$, and $e_{iA}$ are non-zero, absolute temperature units are assumed for all coefficients. If $b_{iA}$, $c_{iA}$, and $e_{iA}$ are all zero, the others are interpreted in input units. The temperature limits are always interpreted in input units.

†† If $a_{iA}$ is missing, $\ln \dfrac{H_{iA}}{\gamma_{iA}^{\infty}}$ is set to zero and the weighting factor $w_A$ is renormalized.

# 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 Free-Water Immiscibility Simplification in Free-Water and Three-Phase Calculations for details.

The expression for the liquid mole fraction of water in the $i$th hydrocarbon species is:

$$\ln x_{wi} = C_{1i} + \frac{C_{2i}}{T} + C_{3i}T \text{ for } C_{4i} \leq T \leq C_{5i}$$

No extrapolation is used with this equation.

The parameters for about 60 components are stored in the Aspen Physical Property System pure component databank.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| WATSOL/1 | $C_{1i}$ | fcn($T_{bi}$, $SG_i$, $M_i$) | — | -10.0 | 33.0 | — |
| WATSOL/2 | $C_{2i}$ | fcn($T_{bi}$, $SG_i$, $M_i$) | — | -10000.0 | 3000.0 | TEMPERATURE † |
| WATSOL/3 | $C_{3i}$ | 0 | — | -0.05 | 0.05 | TEMPERATURE † |
| WATSOL/4 | $C_{4i}$ | 0 | — | 0.0 | 500 | TEMPERATURE † |
| WATSOL/5 | $C_{5i}$ | 1000 | — | 4.0 | 1000 | TEMPERATURE † |

† Absolute temperature units are assumed for elements 2 through 5.

# Hydrocarbon Solubility

This model calculates solubility of hydrocarbon in a water-rich liquid phase. The model is used automatically when you model a hydrocarbon-water system with the dirty-water option. See Free-Water Immiscibility Simplification in Free-Water and Rigorous Three-Phase Calculations for details.

The expression for the liquid mole fraction of the $i$th hydrocarbon species in water is:

$$\ln x_{wi} = C_{1i} + \frac{C_{2i}}{T} + C_{3i}T \text{ for } C_{4i} \leq T \leq C_{5i}$$

No extrapolation is used with this equation.

The parameters for about 40 components are stored in the Aspen Physical Property System pure component databank.

| Parameter Name/ Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| HCSOL/1 | $C_{1i}$ | fcn(carbon number) † | — | -1000.0 | 1000.0 | — |
| HCSOL/2 | $C_{2i}$ | 0 | — | -100000.0 | 100000.0 | TEMPERATURE †† |
| HCSOL/3 | $C_{3i}$ | 0 | — | -100.0 | 100.0 | TEMPERATURE †† |
| HCSOL/4 | $C_{4i}$ | 0 | — | 0.0 | 500 | TEMPERATURE |
| HCSOL/5 | $C_{5i}$ | 1000 | — | 4.0 | 1000 | TEMPERATURE |

† For Hydrocarbons and pseudocomponents, the default values are estimated by the method given by API Procedure 9A2.17 at 25 C.

†† Absolute temperature units are assumed for elements 2 and 3. The temperature limits are always interpreted in user input units.

### Reference

C. Tsonopoulos, Fluid Phase Equilibria, 186 (2001), 185-206.

# Other Thermodynamic Property Models

The Aspen Physical Property System has some 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
- Quadratic Mixing Rule

## Cavett

The general form for the Cavett model is:

$$\left( H_i^{*,l} - H_i^{*,ig} \right) = fcn\left( T, T_{ci}, p, p_{ci}, Z_{\lambda i}^{*} \right)$$

$$\left( H_m^{l} - H_m^{ig} \right) = \sum_i x_i \left( H_i^{*,l} - H_i^{*,ig} \right)$$

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| TC | $T_{ci}$ | — | — | 5.0 | 2000.0 | TEMPERATURE |
| PC | $p_{ci}$ | — | — | $10^5$ | $10^8$ | PRESSURE |
| DHLCVT | $Z_{\lambda,i}^{\infty}$ | ZC | X | 0.1 | 0.5 | — |

# Barin Equations for Gibbs Energy, Enthalpy, Entropy, and Heat Capacity

The following equations are used when parameters from the Aspen Physical Property System inorganic databank are retrieved.

- Gibbs energy:

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

- Enthalpy:

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

- Entropy:

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

- Heat capacity:

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

$\alpha$ 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.) When the temperature is outside all these temperature ranges, linear extrapolation of properties versus $T$ is performed using the slope at the end of the nearest temperature bound.

The four properties $C_p$, $H$, $S$, and $G$ are interrelated as a result of the thermodynamic relationships:

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

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

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

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.

The Aspen Physical Property System has other models which can be used to calculate temperature-dependent properties which the BARIN equations can

calculate. The Aspen Physical Property System uses the parameters in THRSWT to determine which model is used. See Pure Component Temperature-Dependent Properties for details.

| If this parameter is 200 | Then the BARIN equations are used to calculate |
|---|---|
| THRSWT/3 | Liquid vapor pressure |
| THRSWT/5 | Solid heat capacity |
| THRSWT/6 | Liquid heat capacity |
| THRSWT/7 | Ideal gas heat capacity |

## Solid Phase

The parameters in range $n$ are valid for temperature: $T_{n,l}^{s} < T < T_{n,h}^{s}$

When you specify this parameter, be sure to specify at least elements 1 through 3.

| Parameter Name † /Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPSXP$n$/1 | $T_{n,l}^{s}$ | — | x | — | — | TEMPERATURE |
| CPSXP$n$/2 | $T_{n,h}^{s}$ | — | x | — | — | TEMPERATURE |
| CPSXP$n$/3 | $a_{n,i}^{s}$ | — | x | — | — | †† |
| CPSXP$n$/4 | $b_{n,i}^{s}$ | 0 | x | — | — | †† |
| CPSXP$n$/5 | $c_{n,i}^{s}$ | 0 | x | — | — | †† |
| CPSXP$n$/6 | $d_{n,i}^{s}$ | 0 | x | — | — | †† |
| CPSXP$n$/7 | $e_{n,i}^{s}$ | 0 | x | — | — | †† |
| CPSXP$n$/8 | $f_{n,i}^{s}$ | 0 | x | — | — | †† |
| CPSXP$n$/9 | $g_{n,i}^{s}$ | 0 | x | — | — | †† |
| CPSXP$n$/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: $T_{n,l}^{l} < T < T_{n,h}^{l}$

When you specify this parameter, be sure to specify at least elements 1 through 3.

| Parameter Name † /Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPLXP$n$/1 | $T_{n,l}^{l}$ | — | x | — | — | TEMPERATURE |
| CPLXP$n$/2 | $T_{n,h}^{l}$ | — | x | — | — | TEMPERATURE |
| CPLXP$n$/3 | $a_{n,i}^{l}$ | — | x | — | — | †† |
| CPLXP$n$/4 | $b_{n,i}^{l}$ | 0 | x | — | — | †† |
| CPLXP$n$/5 | $c_{n,i}^{l}$ | 0 | x | — | — | †† |
| CPLXP$n$/6 | $d_{n,i}^{l}$ | 0 | x | — | — | †† |
| CPLXP$n$/7 | $e_{n,i}^{l}$ | 0 | x | — | — | †† |
| CPLXP$n$/8 | $f_{n,i}^{l}$ | 0 | x | — | — | †† |

| Parameter Name †/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPLXP$n$/9 | $g_{n,i}^{l}$ | 0 | x | — | — | †† |
| CPLXP$n$/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: $T_{n,l}^{ig} < T < T_{n,h}^{ig}$

When you specify this parameter, be sure to specify at least elements 1 through 3.

| Parameter Name †/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| CPIXP$n$/1 | $T_{n,l}^{ig}$ | — | x | — | — | TEMPERATURE |
| CPIXP$n$/2 | $T_{n,h}^{ig}$ | — | x | — | — | TEMPERATURE |
| CPIXP$n$/3 | $a_{n,i}^{ig}$ | — | x | — | — | †† |
| CPIXP$n$/4 | $b_{n,i}^{ig}$ | 0 | x | — | — | †† |
| CPIXP$n$/5 | $c_{n,i}^{ig}$ | 0 | x | — | — | †† |
| CPIXP$n$/6 | $d_{n,i}^{ig}$ | 0 | x | — | — | †† |
| CPIXP$n$/7 | $e_{n,i}^{ig}$ | 0 | x | — | — | †† |
| CPIXP$n$/8 | $f_{n,i}^{ig}$ | 0 | x | — | — | †† |
| CPIXP$n$/9 | $g_{n,i}^{ig}$ | 0 | x | — | — | †† |
| CPIXP$n$/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 for more information.

Option codes can improve the performance of this model when using mixed solvents and Henry components. See Option Codes for Enthalpy Models for details.

| Parameter Name | Applicable Components | Symbol | Default | Units |
|---|---|---|---|---|
| IONTYP | Ions † | Ion | 0 | — |
| SO25C | Cations | $S_c^{\infty,aq}$ (T=298) | — | MOLE-ENTROPY |
| | Anions | $S_a^{\infty,aq}$ (T=298) | — | MOLE-ENTROPY |
| DHAQFM | Ions, Molecular Solutes †† | $\Delta_f H_k^{\infty,aq}$ | — | MOLE-ENTHALPY |
| CPAQ0 | Ions, Molecular Solutes †† | $C_{p,k}^{\infty,aq}$ | — | HEAT-CAPACITY |
| DHFORM | Molecular Solutes †† | $\Delta_f H_i^{*,ig}$ | — | MOLE-ENTHALPY |
| | Water, Solvents | $\Delta_f H_w^{*,ig}$ | — | MOLE-ENTHALPY |
| CPIG | Molecular Solutes | $C_{p,i}^{*,ig}$ | — | ††† |
| | Water, Solvents | $C_{p,w}^{*,ig}$ | — | ††† |

† IONTYP is not needed if CPAQ0 is given for ions.

†† DHFORM is not used if DHAQFM and CPAQ0 are given for molecular solutes (components declared as Henry's components). If CPAQ0 is missing, DHFORM and Henry's constants are used to calculate infinite dilution enthalpy for solutes.

††† The unit keywords for CPIG are TEMPERATURE and HEAT-CAPACITY. If CPIG/10 or CPIG/11 is non-zero, then absolute temperature units are assumed for CPIG/9 through CPIG/11. Otherwise, user input temperature units are used for all elements of CPIG. User input temperature units are always used for other elements of CPIG.

# 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.)

$$\mu_w^{\bullet} = \mu_w^{\bullet,ig} + \left( \mu_w^{\bullet} - \mu_w^{\bullet,ig} \right)$$

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. Subscript $k$ refers to any ion or molecular solute. If polynomial model parameters are not available, it is calculated from the Criss-Cobble model for ionic solutes:

$$\mu_k^{\infty} = H_k^{\infty} - TS_k^{\infty} + RT\ln\left(\frac{1000}{M_w}\right)$$

$$H_k^{\infty} = \Delta_f H_k^{\infty,aq} + \int_{298.15}^{T} \frac{C_{p,k}^{\infty,aq}}{T} dT$$

$$S_k^{\infty} = \frac{\Delta_f H_k^{\infty,aq} - \Delta_f G_k^{\infty,aq}}{298.15} + \int_{298.15}^{T} \frac{C_{p,k}^{\infty,aq}}{T} dT$$

Because $\Delta_f H_k^{\infty,aq}$ and $\Delta_f G_k^{\infty,aq}$ are based on a molality scale, and $\mu_k^{\infty}$ is based on mole fraction scale, the term $RT\ln(1000/M_w)$ is added.

For molecular solutes, $\mu_k^{\infty}$ is calculated from Henry's law:

$$\mu_k^{\infty} = \mu_k^{\bullet,ig} + RT\ln\left(\frac{H_{k,w}}{P_{ref}}\right)$$

$G^{*E}$ is calculated from the electrolyte NRTL activity coefficient model.

See the Criss-Cobble model and Henry's law model for more information.

Option codes can improve the performance of this model when using mixed solvents and Henry components. See Option Codes for Gibbs Energy Models for details.

| 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, Solvents | $\Delta_f G_w$ | — | MOLE-ENTHALPY |

| Parameter Name | Applicable Components | Symbol | Default | Units |
|---|---|---|---|---|
| CPIG | Molecular Solutes | $C_{p,i}^{*,ig}$ | — | ††† |
| | Water, Solvents | $C_{p,w}^{*,ig}$ | — | ††† |

† IONTYP and SO25C are not needed if CPAQ0 is given for ions.

†† DGFORM is not needed if DHAQFM and CPAQ0 are given for molecular solutes.

††† The unit keywords for CPIG are TEMPERATURE and HEAT-CAPACITY. If CPIG/10 or CPIG/11 is non-zero, then absolute temperature units are assumed for CPIG/9 through CPIG/11. Otherwise, user input temperature units are used for all elements of CPIG. User input temperature units are always used for other elements of CPIG.

# Liquid Enthalpy from Liquid Heat Capacity Correlation

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

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

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

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

Where:

| | | |
|---|---|---|
| $H_i^{*,ig}$ | = | Ideal gas enthalpy |
| $H_i^{*,v} - H_i^{*,ig}$ | = | Vapor enthalpy departure from equation of state |
| $\Delta_{vap} H_i^{*,l}$ | = | Heat of vaporization from Watson/DIPPR/IK-CAPE model |
| $T^{ref}$ | = | Reference temperature, specified by user. Defaults to 298.15 K |

See DIPPR/IK-CAPE Liquid Heat Capacity for parameter requirement and additional details.

# Enthalpies Based on Different Reference States

Two property methods, WILS LR and WILS GLR, are available to calculate enthalpies based on different reference states. The WILS LR property method is based on saturated liquid reference state for all components. The WILS GLR property method allows both ideal gas and saturated liquid reference states.

These property methods use an enthalpy method that optimizes the accuracy tradeoff between liquid heat capacity, heat of vaporization, and vapor heat capacity at actual process conditions. This highly recommended method

eliminates many of the problems associated with accurate thermal properties for both phases, especially the liquid phase.

The liquid enthalpy of mixture is calculated by the following equation (see the table labeled Liquid Enthalpy Methods):

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

Where:

| | | |
|---|---|---|
| $H_m^{ig}$ | = | Enthalpy of ideal gas mixture |
| | = | $\sum_i x_i H_i^{*,ig}$ |
| $H_i^{*,ig}$ | = | Ideal gas enthalpy of pure component $i$ |
| $(H_m^l - H_m^{ig})$ | = | 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 $i$ |
| $\Delta_{vap}H_i^*(T_i^{con,l})$ | = | Heat of vaporization of component $i$ at temperature of $T^{con,l}$ |
| $\Delta H_{v,i}^*(T_i^{con,l}, p_i^{*,l})$ | = | Vapor enthalpy departure of component $i$ at the conversion temperature and vapor pressure $p_i^{*,l}$ |
| $p_i^{*,l}$ | = | Liquid vapor pressure of component $i$ |
| $C_{p,i}^{*,ig}$ | = | Ideal gas heat capacity of component $i$ |

$T_i^{con,l}$ is the temperature at which one crosses from liquid state to the vapor state. This is a user defined temperature that defaults to the system temperature $T$. $T_i^{con,l}$ may be selected such that heat of vaporization for component $i$ at the temperature is most accurate.

The vapor enthalpy is calculated from ideal gas enthalpy as follows:

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

Where:

| | | |
|---|---|---|
| $\Delta H_{v,i}^*(T, P)$ | = | Vapor enthalpy departure of pure component $i$ at the system temperature and pressure |

The liquid heat capacity and the ideal gas heat capacity can be calculated from the ASPEN, DIPPR, IK-CAPE, or BARIN models. The heat of vaporization can be calculated from the Watson/DIPPR/IK-CAPE model. The enthalpy departure is obtained from an equation-of-state.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| RSTATE † | — | 2 | — | — | — | — |
| TREFHL | $T_i^{ref,l}$ | †† | — | — | — | TEMPERATURE |
| DHLFRM | $H_i^{ref,l}$ | 0 | — | — | — | MOLE ENTHALPY |
| TCONHL | $T_i^{con,l}$ | $T$ | — | — | — | TEMPERATURE |

† Enthalpy reference state given by 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:

$$H_i^{*,l} = H_i^{ref,ig} + \int_{T_i^{ref,ig}}^{T_i^{con,ig}} C_{p,i}^{*,ig} dT + \Delta H_{v,i}^*\left(T_i^{con,ig}, p_i^{*,l}\right) - \Delta_{vap}H_i^*\left(T_i^{con,ig}\right) + \int_{T_i^{con,ig}}^{T} C_{p,i}^{*,l} dT$$

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 | $T_i^{con,ig}$ | $T$ | — | — | — | 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 $\bar{V}^o$, heat capacity $\bar{C}_p^o$, entropy $\bar{S}^o$, enthalpy of formation $\Delta \bar{H}^o$, and Gibbs energy of formation $\Delta \bar{G}^o$ at infinite dilution in aqueous phase are:

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

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

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

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

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

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) |

**Note:** Reduced temperature $T_r$ is always calculated using absolute temperature units.

| Parameter Name/Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| AHGPAR/1, ... , 4 | $a_1, ..., a_4$ | 0 | — | — | — | — |
| CHGPAR/1, ... , 2 | $c_1, c_2$ | x | — | — | — | — |
| DHAQHG | $\Delta \overline{H}_f^o$ | 0 | — | $-0.5 \times 10^{10}$ | $0.5 \times 10^{10}$ | MOLE-ENTHALPY |
| DGAQHG | $\Delta \overline{G}_f^o$ | 0 | — | $-0.5 \times 10^{10}$ | $0.5 \times 10^{10}$ | MOLE-ENTHALPY |
| S25HG | $\overline{S}_{T_r P_r}^o$ | 0 | — | $-0.5 \times 10^{10}$ | $0.5 \times 10^{10}$ | MOLE-ENTROPY |
| OMEGHG | $\omega_{T_r P_r}$ | 0 | — | $-0.5 \times 10^{10}$ | $0.5 \times 10^{10}$ | MOLE-ENTHALPY |

If pressure is under 200 bar, AHGPAR may not be required.

## References

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# Quadratic Mixing Rule

The quadratic mixing rule is a general-purpose mixing rule which can be applied to various properties. For a given property $Q$, with $i$ and $j$ being components, the rule is:

$$Q = \sum_i x_i Q_i + \sum_i x_i \sum_j x_j K_{ij} \left( Q_i Q_j \right)^{0.5}$$

The pure component properties $Q_i$ and $Q_j$ are calculated by the default model for that property, unless modified by option codes. Composition $x_i$ and $x_j$ is in mole fraction unless modified by option codes. $K_{ij}$ is a binary parameter specific to the mixing rule for each property. A variation on the equation using the logarithm of the property is used for viscosity.