User Guide for

Models and Physical Properties

Infochem/KBC Advanced Technologies plc

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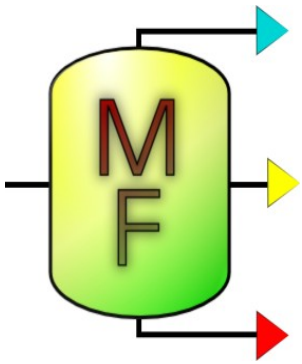

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Overview

Introduction

Multiflash is an advanced software package for performing complex equilibrium calculations quickly and reliably. The main utility is a multiple phase equilibrium algorithm that is interfaced to Infochem's package of thermodynamic models and a number of physical property data banks.

The purpose of this guide is to provide more detailed descriptions of the models available in Multiflash than you will find in our main User Guide. The correlation equations for storing pure component properties in our physical property databanks will also be described.

This section defines what a model is in terms of the Multiflash nomenclature, what models are available and when you might wish to use them.

What types of model are available?

Within the context of Multiflash, a model is a mathematical description of how one or more thermodynamic or transport properties of a fluid or solid will depend on pressure, temperature or composition.

The key thermodynamic property calculation carried out within Multiflash is the determination of phase equilibrium. This is based on the fundamental relationship that at equilibrium the fugacity of a component is equal in all phases. For a simple vapour-liquid system

$$f_i^v = f_i^l$$

where f_i^v is the fugacity of component i in the vapour phase and f_i^l is the fugacity of component i in the liquid phase.

The models used in Multiflash to represent the fugacities from the phase equilibrium relationship in terms of measurable state variables (temperature, pressure, enthalpy, entropy, volume and internal energy) fall into two groups, equation of state methods and activity coefficient methods. The basis of each of these methods is described below.

With an equation of state method, all thermal properties for any fluid phase can be derived from the equation of state. With an activity coefficient method the vapour phase properties are derived from an equation of state, whereas the liquid properties are determined from the summation of the pure component properties to which a mixing term or an excess term has been added.

Multiflash may also be used to calculate the phase equilibrium of systems containing solid phases, either mixed or pure. These may occur either when a normal fluid freezes or may be a particular solid phase such as a hydrate, wax or asphaltene. Models used to represent these solids are discussed below.

The transport properties of a phase (viscosity, thermal conductivity and surface tension) are derived from semi-empirical models, which will be discussed later.

Equation of state methods

An equation of state describes the pressure, volume and temperature (PVT) behaviour of pure components and mixtures. Most equations of state have different terms to represent the attractive and repulsive forces between molecules. Any thermodynamic property, such as fugacity coefficients and enthalpies, can be calculated from an equation of state relative to the perfect gas properties of the same mixture at the same conditions.

In the equation of state method the partial pressure of a component i in a gas mixture is

$$p_i = y_i p .$$

The fugacity of a component in an perfect gas mixture is equal to its partial pressure; the fugacity in a real mixture is the effective partial pressure

$$f_i^v = \varphi_i^v y_i p$$

where φ_i^v is the fugacity coefficient. For a vapour at moderate pressures φ_i^v is close to unity.

Similarly for a liquid

$$f_i^l = \varphi_i^l x_i^l p$$

Although since a liquid differs considerably from an perfect gas the fugacity coefficients for a liquid are very different from unity.

Activity coefficient methods

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

$$f_i^l = x_i f_i^{*,l}$$

The ideal solution assumes that all molecules in the liquid solution are identical in size and are randomly distributed. This assumption is valid for mixtures made up of molecules of similar size and

type, but for mixtures of unlike molecules you must expect varying degrees of non-ideality. The activity coefficient, γ_i, represents the deviation of the mixture from ideality, as defined by the ideal solution.

The fugacity coefficients for the activity coefficient equations are calculated from the standard relationship:

$$\ln\varphi_i = \ln\gamma_i + \ln p_i^{sat} + \ln\varphi_i^{sat} - \ln p + \Pi_i$$

where γ_i is the activity coefficient of component i which is derived from the excess Gibbs energy as follows:

$$\ln\gamma_i = \frac{\partial G^E}{\partial n_i}.$$

p_i^{sat} is the saturated vapour pressure of component i, φ_i^{sat} is the fugacity coefficient of the pure saturated vapour of component i (calculated from the gas phase model associated with the activity coefficient equation) and p is the total pressure.

The Poynting correction, Π_i, corrects the fugacity coefficient from the standard state pressure (*i.e.* the saturation pressure) to the system pressure. It is evaluated on the assumption of ideality, *i.e.* assuming that there is zero excess volume of mixing, and that the liquid is incompressible:

$$\Pi_i = \frac{(p - p_i^{sat})v_i^{sat}}{RT}$$

where v_i^{sat} is the saturated liquid volume of component i.

Thermodynamic properties from an Equation of State

Introduction

Any thermodynamic property can be calculated with an equation of state. This section present the general expressions used in Multiflash to calculate thermodynamic properties, like enthalpy and fugacity coefficients from equations of state. Some properties, like enthalpy and entropy are calculate directly from the equation of state, while others like the Gibbs energy are calculated as combinations of other properties.

Enthalpy

In Multiflash the enthalpy is calculated as

$$H = H_{ref} + H_{pg} + H_{res} ,$$

where:

H_{ref} is the (arbitrary) enthalpy value in a reference state to be defined.

H_{pg} is the perfect gas contribution to the enthalpy, given by:

$$H_{pg} = \int_{T_{ref}}^{T} C_{P,pg}\, dT ,$$

where $C_{P,pg}$ is the perfect gas heat capacity;

H_{res} is the residual enthalpy, which is calculated from the thermodynamic model specified for thermal properties, using the standard thermodynamic relation:

$$H_{res} = PV - RT + \int_{\infty}^{V} \left[\left(\frac{\partial P}{\partial T} \right)_V - P \right] dV .$$

The absolute value of enthalpy has no physical meaning but enthalpy differences are measurable quantities, therefore H_{ref} can be chosen at will. Multiflash has two possible reference states that are user selectable:

1. ‘Compound’ datum (default): The enthalpy of each pure component in the perfect gas state at 298.15 K and 1 atm is set to zero. This is done by setting:

$$H_{ref} = -H_{pg}^{298},$$

where H_{pg}^{298} is the value of H_{pg} at T = 298.15 K.

2. ‘Elements’ datum: The enthalpy of each element is set to zero in the perfect gas state at 298.15K and 1 atm., which is done by setting:

$$H_{ref} = \Delta H_f^o - H_{pg}^{298},$$

where ΔH_f^o is the standard enthalpy of formation of the compounds in the perfect gas state at 298.15 K and 1 atm.

This datum produces enthalpy values that are much larger numerically than the ‘compound’ datum but enthalpy differences between two states are the same. When calculating chemical reaction equilibrium the ‘elements’ datum must be used because it is the elemental entities that are conserved rather than the molecular entities.

The overall enthalpy is obtained by multiplying the mole numbers of each phase with the enthalpy of each phase, and summing over all phases:

$$H = \sum_{j}^{NP} n_j H_j .$$

Entropy

The entropy is in Multiflash calculated as:

$$S = S_{ref} + S_{pg} + S_{res},$$

where:

S_{ref} is the (arbitrary) entropy value in a reference state to be defined.

S_{pg} is the perfect gas contribution to the entropy, given by:

$$S_{pg} = \int_{T_{ref}}^{T} \frac{C_{P,pg}}{T} dT,$$

where $C_{P,pg}$ is the perfect gas heat capacity;

S_{res} is the residual entropy at specified T and P, which is calculated from the thermodynamic model specified for thermal properties, using the standard thermodynamic relation:

$$S_{res} = \int_{0}^{P} \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV + R \ln Z,$$

where Z is the compressibility factor:

$$Z = \frac{P V}{n R T} .$$

Although the absolute entropy can be argued to have a physical interpretation, in practise, it is entropy differences that are experimentally accessible and S_{ref} can be chosen at will. Multiflash has three possible reference states that are user selectable:

1. 'Compound' datum (default): The entropy of each pure component in the perfect gas state at 298.15 K and 1 atm is set to zero. This is done by setting:

$$S_{ref} = -S_{pg}^{298} ,$$

where S_{pg}^{298} is the value of S_{pg} at 298.15 K.

2. 'Elements' datum: The entropy of each element is set to zero in the perfect gas state at 298.15K and 1 atm, by setting:

$$S_{ref} = \Delta S_f^o - S_{pg}^{298} ,$$

where ΔS_f^o is the entropy of formation at 298.15 K and 1 atm.

This datum produces values that are much larger numerically than the 'compound' datum but entropy differences between two states are the same. When calculating chemical reaction equilibrium the 'elements' datum must be used.

3. 'Standard' datum (sometimes called the 'third-law or 'absolute' entropy): The reference entropy is chosen so that the entropy of each component in the perfect gas state at 298.15K and 1 atm is equal to the standard entropy of that component. This is done by setting:

$$S_{ref} = S^o - S_{pg}^{298}$$

The standard entropy, S^o is relative to a zero value at absolute zero. The 'standard' datum may also be used in chemical reaction analysis since the results are equivalent to the 'elements' datum.

The overall entropy is obtained by multiplying the mole numbers of each phase with the entropy of each phase, and summing over all phases.

Fugacity coefficients

The fugacity coefficient, $\hat{\phi}_i$ is the ratio between the fugacity and the partial pressure of a given component:

$$\hat{\phi}_i = \frac{\hat{f}_i}{P x_i}$$

It is calculated as:

$$\ln \hat{\phi}_i = \frac{-1}{RT} \int_{\infty}^{V} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln Z$$

Gibbs Energy and Internal Energy

The internal energy, U is calculated from the enthalpy:

$$U = H - PV$$

and the Gibbs free energy, G is calculated from the enthalpy and entropy

$$G = H - TS$$

Heat Capacity, constant pressure

The heat capacity at constant pressure, C_P is equal to the temperature derivative of the enthalpy at constant pressure:

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P .$$

It is calculated as the sum of a perfect gas and a residual contribution:

$$C_P = C_{P,pg} + C_{P,res} = C_{P,pg} + \left(\frac{\partial H_{res}}{\partial T} \right)_P ,$$

where H_{res} is defined under enthalpy and $C_{P,pg}$ is the perfect gas heat capacity.

A number of correlations for the perfect gas heat capacity are stored in the Infodata databank, but user-defined correlations may be entered . Which correlation from the databank is used depends on the component.

As for enthalpy the overall heat capacity is obtained by multiplying the heat capacity of each phase with the corresponding mole numbers.

Heat Capacity, constant volume

C_V is the heat capacity at constant volume, given by the temperature derivative of the internal energy at constant volume:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V .$$

More conveniently it can be calculated from the constant pressure heat capacity and the temperature and pressure derivatives of V:

$$C_V = C_P + T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial V}{\partial P} \right)_T^{-1} .$$

As for enthalpy the overall heat capacity is obtained by multiplying the enthalpy of each phase with the corresponding mole numbers.

Isothermal compressibility

The quantity isothermal compressibility, β, is the response of a material in terms of volume change when pressure is applied at constant temperature.

It is determined using the following expression:

$$\beta = \frac{-1}{V}\frac{\partial V}{\partial p}\bigg|_{T=const}$$

Where V is the volume, p is the pressure and T is the temperature.

The inverse of the compressibility is called the bulk modulus.

Isobaric expansivity or thermal expansion

The quantity isobaric expansivity, α, is the response of a material in terms of volume change when temperature changes at constant pressure.

It is determined using the following expression:

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\bigg|_{p=const}$$

Where V is the volume, p is the pressure and T is the temperature.

Joule Thompson coefficient

The Joule-Thompson effect describes the behaviour of the temperature of a mixture when it is subjected to pressure changes without energy transfer to the surroundings.

This is quantified by the Joule-Thompson coefficient (μ_{JT}) given by:

$$\mu_{JT} = \frac{\partial T}{\partial P}\bigg|_{H=const} = \frac{V}{C_P}(\alpha T - 1)$$

The quantity α is the isobaric expansivity described above. The values V, P and C_P are volume, pressure and heat capacity at constant pressure, respectively.

Activity Coefficient

The activity coefficient of a component is defined as the activity of that component divided by the mole fraction:

$$\gamma_i \equiv \frac{a_i(T, P, \boldsymbol{n})}{x_i},$$

and it is in Multiflash calculated as the fugacity of the component in the mixture divided by the pure component fugacity at the same temperature and pressure:

$$\gamma_i = \frac{\hat{\phi}_i(T, P, \boldsymbol{n})}{\phi_i(T, P)} .$$

Speed of Sound

The Speed of Sound of each phase is calculated as:

$$c = \sqrt{\frac{C_P V^2}{-C_V M_w \frac{\partial V}{\partial P}}} ,$$

where M_w is the molecular weight of the phase

For multiple phases the overall speed of sound is estimated using the equation of Wallis. Reference: G. B. Wallis: 'One dimensional two-phase flow', McGraw-Hill, 1969.

$$c = \frac{V_{mix}}{\sqrt{-\sum_i^{NP} n_i \frac{C_V \frac{\partial V}{\partial P}}{C_P} \times \sum_i^{NP} n_i Mn_i}}$$

Equations of state provided in Multiflash

When to use equation of state models

Equations of state (EOS) can be used over wide ranges of temperature and pressure, including the sub-critical and supercritical regions. They are frequently used for ideal or slightly non-ideal systems such as those related to the oil and gas industry where modelling of hydrocarbon systems, perhaps containing light gases such as H_2S, CO_2 and N_2, is the norm. Equation of state methods do not necessarily represent highly non-ideal chemical systems, such as alcohol-water, well. For this type of system, at low pressure, an activity coefficient approach is preferable but at higher pressure you may need to use an equation of state with excess Gibbs energy mixing rules, see “Mixing Rules” on page 18.

All equations of state will describe any system more accurately when binary interaction parameters (BIPs) have been derived from the regression of experimental phase equilibrium data. BIPs are adjustable factors, which are used to alter the predictions from a model until these reproduce as closely as possible the experimental data.

As mentioned earlier the thermal properties of any fluid phase can be derived from an equation of state. However, one property, which is often poorly represented by the simpler equations of state, is the liquid density. Multiflash offers enhanced versions of both the Redlich-Kwong-Soave (RKS) and Peng-Robinson (PR) cubic equations of state where the equation of state parameters can be fitted to reproduce both the saturated vapour pressure using a databank correlation and the saturated liquid density at 298K or T_r=0.7 (Peneloux method). These are referred to in Multiflash as the advanced version of the particular equation of state.

Further guidance on the use of specialised equations of state is given in the following sections.

Perfect gas equation of state

The perfect gas equation of state is defined as

$$p = \frac{N\,RT}{V}\,.$$

This model is normally used in conjunction with an activity coefficient method when the latter is used to model the liquid phase. It could also be used to describe the behaviour of gases at low pressure.

Peng-Robinson equation of state

The Peng-Robinson (PR) equation (D.-Y. Peng and D. B. Robinson, Ind. Eng. Chem. Fundam., **15**, 1, (1976)).is a cubic equation of state. It is described by

$$p = \frac{NRT}{V-b} + \frac{a}{V^2 + 2bV - b^2}$$

where a and b are derived from functions of pure component critical temperatures and pressures and acentric factor.

$$a_i = a_{ci}\left(1 + \kappa_i\left(1 - \sqrt{T/T_{ci}}\right)\right)^2$$

$$a_{ci} = 0.45724\frac{R^2 T_{ci}^2}{p_{ci}}$$

and

$$\kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

except for water when $\sqrt{T/T_{ci}} < 0.85$ where the following alternative relation is used:

$$a_i = a_{ci}\left(1.0085677 + 0.82154\left(1 - \sqrt{T/T_{ci}}\right)\right)^2$$

The standard (Van der Waals 1-fluid) mixing rules are:

$$N = \sum_i n_i$$

$$a = \sum_{ij} \sqrt{a_i a_j}\,(1 - k_{ij})\,n_i n_j$$

$$b = \sum_i b_i n_i$$

$$b_i = 0.07780\frac{RT_{ci}}{p_{ci}}$$

k_{ij} is usually referred to as a binary interaction parameter, the use of such parameters is discussed in a later section.

Peng-Robinson 1978 (PR78) equation of state

The 1978 revised version of the Peng-Robinson EOS (D. B. Robinson and D.-Y. Peng, GPA Research Report 28, Gas Processors Association, Tulsa, (1978)) has a different treatment for the parameter κ. If the acentric factor $\omega < 0.49$ the same expression is used as before:

$$\kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

but, if $\omega \geq 0.49$ the following relationship is used:

$$\kappa_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.01666\omega_i^3$$

The new expression removes a defect in the original equation where heavy components with higher acentric factors become more volatile than components with somewhat lower acentric factors. However, for any mixture containing components with acentric factors greater than 0.49 the PR78 equation will give different results and must therefore be treated as a different model.

Redlich-Kwong (RK) equation

The Redlich-Kwong EOS (O. Redlich and J. N. S.. Kwong, Chem. Rev., **44**, 233, (1949)) and its variants are further examples of simple cubic equations of state.

It has the form:

$$p = \frac{NRT}{V - b} + \frac{a}{V(V + b)}$$

where

$$a_i = a_{ci}\sqrt{T_{ci}/T}$$

$$a_{ci} = 0.42748\frac{R^2 T_{ci}^2}{p_{ci}}$$

The standard (Van der Waals 1-fluid) mixing rules are:

$$N = \sum_i n_i$$

$$a = \sum_{ij} \sqrt{a_i a_j}(1 - k_{ij}) n_i n_j$$

$$b = \sum_i b_i n_i$$

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

Redlich-Kwong-Soave (RKS) equation

The RKS EOS (G. Soave, Chem. Eng. Sci., **27**, 1197, (1972)) .has the same form and mixing rules as the RK equation but the a parameter is a function of temperature.

$$a_i = a_{ci}\left(1+\kappa_i\left(1-\sqrt{T/T_{ci}}\right)\right)^2$$

where:

$$\kappa_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2$$

and for API variant (M. S. Graboski and T. E. Daubert, Ind. Eng. Proc. Des. Dev., **17**, 443, (1978)):

$$a_i = a_{ci}\left(1+\kappa_i\left(1-\sqrt{T/T_{ci}}\right)\right)^2$$

where:

$$\kappa_i = 0.48508 + 1.5517\omega_i - 0.15613\omega_i^2$$

except for hydrogen, which in the API variant is given by:

$$a_i = 1.202 a_{ci} \exp\left(-0.30228\frac{T}{T_{ci}}\right)$$

Zudkevitch-Joffe (ZJ)

The ZJ EOS is based on the original version of Redlick-Kwong (RK) eos (D. Zudkevitch and J. Joffe, AIChEJ, **16**, 112 (1970).

For the original version of RK, the “a” and “b” parameters are expressed explicitly in terms of the critical temperature and pressure

$$p = \frac{NRT}{V-b} + \frac{a}{V(V+b)}$$

where the a_i and b_i for each component are defined as:

$$b_i = 0.08664\frac{R\,T_c}{p_c}$$

$$a_i = 0.42748\frac{R^2\,T_{ci}^2}{p_{ci}}\sqrt{T_{ci}/T}$$

For the ZJ eos, the a_i and b_i parameters are defined by simultaneously solving the equations of fugacity coefficients along the saturation line and the RKS equation for both vapour and saturated liquid phase, where the required saturation vapour pressure and saturated liquid density are obtained from the correlation of the pure components.

Advanced Equation of state options

The advanced implementation of both the Peng-Robinson and the Redlich-Kwong-Soave equations of state (PRA, PR78A and RKSA models) contain additional non-standard features. These include the ability to match stored values for the liquid density and the saturated vapour pressure and a choice of mixing rule.

The Peneloux density correction

This correlation is used to match the density calculated from the equation of state to that stored in the chosen physical property data system. For light gases, the density is matched at a reduced temperature of 0.7 and the volume correction is assumed constant. For liquid components the volume shift is a function of temperature.

$$c_i = c_{i0} + c_{i1}T + c_{i2}/T$$

$$V = V' - \sum c_i x_i$$

The three coefficients may be stored as part of the pure component data record.

Multiflash usually treats the volume shift as a linear function of temperature; the density is matched at 290.7K and 315.7K so as to reproduce the density and thermal expansivity of liquids over a range of temperatures centred on ambient. However, users may also use the third term and enter the coefficient values directly.

Fitting the vapour pressure curve

The function for a_i is generalised to the following form:

$$a = a_{ci}\left(1 + \kappa_{i1}t_i + \kappa_{i2}t_i^2 + \kappa_{i3}t_i^3 + \kappa_{i4}t_i^4 + \kappa_{i5}t_i^5\right)^2$$

where

$$t_i = 1 - \sqrt{T/T_{ci}}\ .$$

For each component the constants, κ_{i1} to κ_{i5} are fitted by linear regression to the vapour pressure over a range of reduced temperatures corresponding to the stored data. Fewer than 5 coefficients will be fitted if there is insufficient data or if the extrapolation to low temperatures is unrealistic. If the vapour pressure is undefined, the correlation for a_i reverts to the standard equation for that component.

Mixing Rules

For highly non-ideal systems it is often useful to be able to use any Gibbs energy excess model (e.g. UNIQUAC or NRTL) as part of the mixing rule for the equation of state. There are several different ways in which this can be done; Multiflash currently provides options for the MHV2 type mixing rule, the Huron-Vidal type mixing rule, the PSRK mixing rule and the Infochem modification

based on the NRTL equation. The latter is used for modelling the fluid phases in hydrate calculations.

MHV2-type mixing rules:

$$N = \sum_i n_i$$

$$b = \sum_i b_i n_i$$

$$a = -\frac{RTb}{s_1}\left(Q(\alpha) - \frac{s_2 N^2}{Q(\alpha)}\right)$$

$$Q(\alpha) = \frac{G^E}{RT} + \sum_i n_i \left(Q_i(\alpha_i) + \ln\left(\frac{b}{Nb_i}\right)\right)$$

$$Q_i(\alpha_i) = \frac{-\alpha_i s_1 - \sqrt{(\alpha_i s_1)^2 + 4s_2}}{2}$$

For the RKS equation $s_1 = \ln 2$ and $s_2 = 17.25$

For the PR equation $s_1 = \frac{1}{2\sqrt{2}} \ln\left(\frac{2+\sqrt{2}}{2-\sqrt{2}}\right) = 0.623225$ and $s_2 = 20.129$.

Huron-Vidal type mixing rules:

$$N = \sum_i n_i$$

$$b = \sum_i b_i n_i$$

$$a = b\left(-\frac{G^E}{s_1} + \sum_i n_i \left(\frac{a_i}{b_i}\right)\right)$$

For the RKS equation $s_1 = \ln 2$

For the PR equation $s_1 = \frac{1}{2\sqrt{2}} \ln\left(\frac{2+\sqrt{2}}{2-\sqrt{2}}\right) = 0.623225$

PSRK type mixing rules:

$$N = \sum_i n_i$$

$$b = \sum_i b_i n_i$$

$$a = b\left[\frac{G^E}{s_1} + \frac{RT}{s_1}\sum_i n_i \ln\left(\frac{b}{b_i}\right) + \sum_i n_i\left(\frac{a_i}{b_i}\right)\right]$$

$$s_1 = -0.64663$$

Infochem mixing rules:

These mixing rules are similar to the original Huron-Vidal mixing rules apart from the form of the interaction parameters k_{ij}, k_{ji} and α_{ij} which gives a different form of temperature dependence. These rules reduce to the conventional van der Waals mixing rules when $k_{ij} = k_{ji}$ and $\alpha_{ij} = 0$.

$$N = \sum_i n_i$$

$$b = \sum_i b_i n_i$$

$$a = b\sum_i n_i \frac{\sum_j n_j b_j \xi_{ji} G_{ji}}{\sum_j n_j b_j G_{ji}}$$

where:

$$\xi_{ji} = \frac{2\sqrt{a_i a_j}(1 - k_{ji})}{b_i + b_j}$$

and:

$$G_{ji} = \exp\left(\frac{\alpha_{ji}(\xi_{ji} - \xi_{ii})}{RT}\right)$$

Huron-Vidal-Pedersen (HVP) mixing rules:

The HVP mixing rule was first described in JN Kristensen, PL Christensen, KS Pedersen and P. Skovborg "A combined Soave-Redlich-Kwong and NRTL equation for calculating the distribution of methanol between water and hydrocarbon phases". *Fluid Phase Equilibria.* 82, 199-206, 1993. It was designed to extend the validity of cubic equations of state to systems containing methanol. It requires three binary interaction parameters (i.e., $\Delta g_{ij}/R$, $\Delta g_{ji}/R$, and $\alpha_{ij}=\alpha_{ji}$).

The mixing rule can be written as:

$$N = \sum_i n_i$$

$$b = \sum_i b_i n_i$$

$$a = b[(\sum_{i=1} n_i \frac{a_i}{b_i}) - \frac{g^{ex}}{\ln 2}],$$

with

$$g^{ex} = \sum_{i=1} n_i \frac{\sum_{j=1} \Delta g_{ji} b_j n_j \exp\left(\frac{-\alpha_{ji} \Delta g_{ji}}{RT}\right)}{\sum_{j=1} b_j n_j \exp\left(\frac{-\alpha_{ji} \Delta g_{ji}}{RT}\right)}$$

The parameters α_{ij} are dimensionless. On the other hand, it is common in literature to encounter the asymmetric parameters expressed in the form $\Delta g_{ij}/R$ with the units of K. Indeed, Multiflash accepts the asymmetrical parameters in this form (i.e., $\Delta g_{ij}/R$) and with units of K.

If for a given pair of components i-j, the phase behaviour can be accurately described with "classical" WDW k_{ij}, we can obtain the corresponding HVP parameters by setting $\alpha_{ij} = 0$ and using:

$$\Delta g_{ji} = \ln 2 \left[\frac{a_i}{b_i} - 2 \frac{\sqrt{(a_i a_j)}}{b_i + b_j} (1 - k_{ij}) \right]$$

Therefore, the Multiflash GUI is also able to deal with "VDW-like" parameters for the HVP mixing rule.

Finally, if all the pairs of component can be described by classical and symmetric k_{ij}, the HVP mixing rule reduces to the conventional VDW mixing rule.

When to use cubic equations of state

The simple cubic equations of state, PR and RKS, are widely used in engineering calculations. They require limited pure component data and are robust and efficient. Both PR and RKS are used in gas-processing, refinery and petrochemical applications. They will usually give broadly similar results, although if one model has been fitted to experimental data and there are no interaction parameters for the other then the optimised model is always preferable. There is some evidence that RKS gives better fugacities and PR better volumes (densities) but both can be improved if the Peneloux correction is used.

For most applications we would recommend the use of the RKSA (or PRA, PR78A) model sets which use the Peneloux correction, fit *a* to the vapour pressure and use the Van der Waals 1-fluid mixing rules.

RKSA with the Infochem mixing rules is used as part of the hydrate model and provides extra flexibility to represent the highly non-ideal polar systems. It does, however, require suitable BIPs for such systems.

The API variant of RKS is applicable to petroleum systems and mixtures containing hydrogen, while RK may be used instead of perfect gas model for the vapour phase of systems where the liquid phase is being modelled with an activity coefficient model.

Cubic plus association (CPA) model

The CPA model consists of the Redlich-Kwong-Soave equation plus an additional term based on Wertheim's theory that represents the effect of chemical association.

The form of the model is:

$$p = \frac{\sum_i n_i F_i \left(1 - X_i\right)}{V - 0.45b} + \frac{NRT}{V - b} + \frac{a}{V\left(V + b\right)}$$

The parameters a_{ci} and b_i are set for each component to satisfy the critical conditions $\frac{\partial p}{\partial V} = \frac{\partial^2 p}{\partial V^2} = 0$ at the known critical point of that component. The parameter a is a function of temperature given by:

$$a_i(T) = a_{ci}\left(1 + \kappa_{1i} t_i + \kappa_{2i} t_i^2 + \kappa_{3i} t_i^3 + \kappa_{4i} t_i^4 + \kappa_{5i} t_i^5\right)^2$$

where:

$$t_i = 1 - \sqrt{T/T_{ci}}\ .$$

For each component the constants, κ_{0i} to κ_{i5} are fitted by linear regression to the vapour pressure over a range of reduced temperatures corresponding to the stored data. Fewer than 5 coefficients will be fitted if there are insufficient data or if the extrapolation to low temperatures is unrealistic.

The model uses the standard (Van der Waals 1-fluid) mixing rules which are:

$$N = \sum_i n_i$$

$$a = \sum_{ij} \sqrt{a_i a_j}\,(1 - k_{ij}) n_i n_j$$

$$b = \sum_i b_i n_i$$

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

The Wertheim association term is complex and, for a complete discussion, the user should refer to the scientific literature. In summary, the terms X_i are found by simultaneously solving the Wertheim equations, which in the CPA model have the form:

$$\frac{1}{X_i} = 1 + \frac{\sum_j K_{ij} F_j X_j}{V - 0.45b}$$

where F_i are the number of (donor) bonding sites on component i and K_{ij} is the association constant for components i and j.

The CPA model also uses the Peneloux density correction to match the liquid density calculated from the equation of state to that stored in the chosen physical property data system. The volume shift is a linear function of temperature which is set to match the saturated liquid density at two different temperatures. For light gases, a constant volume shift is used that is fitted to the gas's liquid density at a reduced temperature of 0.7.

When to use CPA

The CPA model may be used for hydrate calculations with methanol, ethanol, MEG, DEG, TEG and salt inhibition, as these are the only cases for which parameters are currently provided. Parameters for additional substances may be added in future versions of Multiflash.

PC-SAFT equation of state

The PC-SAFT equation is a development of the SAFT model that has been shown to give good results for a wide range of polar and non-polar substances including polymers. Polymers are one of the most important areas of application of PC-SAFT. The model appears to be one of the most accurate and realistic equations of state currently available for modelling polymer systems.

PC-SAFT stands for the Perturbed Chain Statistical Associating Fluid Theory and it incorporates current ideas of how to model accurately the detailed thermodynamics of fluids within the framework of an equation of state. The mathematical structure is very complex and cannot be conveniently described in a manual. Users are referred to Appendix A of the reference given below.

Reference: *Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules* by Gross and Sadowski in Industrial and Engineering Chemistry Research, **40**, 1244, (2001).

The Multiflash version includes an implementation of the association term of PC-SAFT which is discussed in the paper, *Application of the Perturbed-Chain SAFT Equation of State to Associating Systems* by Gross and Sadowski in Industrial and Engineering Chemistry Research, **41**, 5510, (2002). This paper however does not discuss the mathematical formulation of the association term; this can be found in the following reference.

Reference: *New Reference Equation of State for Associating Liquids* by Chapman, Gubbins, Jackson and Rodosz in Industrial and Engineering Chemistry Research, **29**, 1709, (1990).

The Multiflash implementation follows the same general structure as the association term in the CPA model.

Multiflash also has a version of PC-SAFT with simplified mixing rules as proposed by researchers at the Danish Technical University.

Reference: *Computational and Physical Performance of a Modified PC-SAFT Equation of State for Highly Asymmetric and Associating Mixtures* by von Solms, Michelsen and Kontogeorgis in Industrial and Engineering Chemistry Research, **42**, 1098, (2003).

Polymer Components

Polymers are not well-defined chemical compounds but rather a distribution of chain molecules of varying molecular weight. In Multiflash, polymers must be represented by one or more pseudo components, which must be set up as user-defined components.

Using PC-SAFT, every pseudo component for a given polymer must be assigned the same values of the pure-compound parameters SAFTSIGMA (in metres, *not* Ångstrom units) and SAFTEK. In addition, the SAFTM parameter must be specified. This is normally quoted as a ratio to the molecular weight, so it has to be calculated for each polymer pseudo component knowing the molecular weight. For polystyrene, for example, Gross and Sadowski give the ratio as 0.019, so for a polystyrene pseudo component of molecular weight 100000, the SAFTM parameter should be set to 100000×0.019=1900, etc.

Additionally, the user can define association parameters if the polymer forms hydrogen bonds. These parameters are SAFTBETA which defines the volumetric or entropic parameter, and SAFTEPSILON the energy or enthalpy parameter. Multiflash also provides an extension to the PC-SAFT definition: the user can also supply a heat capacity parameter SAFTGAMMA for the association term. For the association term to be non-zero, the user must also define the parameter SAFTFF which denotes the number of donor bonding sites **per segment** of polymer.

Values of PC-SAFT parameters for polymers can be found in *Modeling Polymer Systems Using the Perturbed-Chain Statistical Associating Fluid Theory Equation of State* by Gross and Sadowski in Industrial and Engineering Chemistry Research, **41**, 1084, (2002) and in *Modeling of polymer phase equilibria using Perturbed-Chain SAFT* by Tumakaka, Gross and Sadowski in Fluid Phase Equilibria, **194-197**, 541, (2002).

Defining Polymers and Copolymers from their Segments

Multiflash also allows the user to define up to four polymer segments which can be used to define any number of homopolymers or copolymers following the method of Tumakaka, Gross and Sadowski described in the reference above.

For each segment the user must define the molecular weight MW and the SAFT parameters SAFTEK and SAFTSIGMA. Optionally, the association parameters SAFTBETA, SAFTEPSILON, optionally SAFTGAMMA and SAFTFF can be defined.

Once a number of segments are defined, the user can then define polymers in terms of the segments as an alternative to the normal method of defining a SAFT component. To define polymer components in this manner, all the user has to do is define the molecular weight MW of the polymer and specify the bond fractions between the segments from which the polymer is constructed. If the polymer is formed from only one type of segment, it is a homopolymer of that segment; if it is formed of two or more types of segment, it is a copolymer. The definition of the bond fractions is given by Tumakaka, Gross and Sadowski,

(although their examples of actual values of bond fractions are not realistic).

All other parameters of the polymer, including the segments fractions, are then internally calculated by Multiflash from the supplied molecular weight and bond fractions. The user can define the BIPs between normal components and/or segments. Note that in the fluid composition, the amounts of the segments must all be set to zero, as the segments are not real components of the mixture.

PSRK equation of state

This model consists of the RKSA equation of state with vapour pressures fitted using Mathias-Copeman parameters (if available), the Peneloux volume correction and the PSRK type mixing rules. The excess Gibbs energy is provided by the PSRK variant of the UNIFAC method. This is the same as the normal VLE UNIFAC model except that the group table has been extended to include a large number of common light gases.

When to use PSRK

The PSRK model is an extension of the UNIFAC method. It is intended to predict the phase behaviour of a wide range of polar mixtures using the solution of groups concept as embodied in UNIFAC. The main benefit of PSRK is that it is able to handle mixtures containing gases much better than UNIFAC and unlike a normal equation of state it can handle polar liquids. This is because (a) it uses an equation of state with an excess Gibbs energy mixing rule thereby avoiding problems of how to handle supercritical components in an activity coefficient equation; (b) the UNIFAC group parameter table has been extended in PSRK to include 32 common light gases.

PSRK-NRTL equation of state

This model is the same as the PSRK model except that the excess Gibbs energy is provided by the NRTL equation. So unlike the PSRK equation, the PSRK-NRTL variant requires that BIPs are provided for the NRTL equation in order to give accurate results. Its advantage is that, provided the BIPs are fitted to relevant phase-equilibrium data, the model can give more accurate predictions than the PSRK equation.

Lee-Kesler (LK) and Lee-Kesler-Plöcker (LKP) equations of state

The LK and LKP methods are 3 parameter corresponding states methods based on interpolating the reduced properties of a mixture between those of two reference substances. The equation for each property is of the form:

$$z^{mix} = z^{(0)} + \frac{\omega}{\omega^{(1)}}\left[z^{(1)} - z^{(0)}\right]$$

where $z^{(0)}$ and $z^{(1)}$ are the compressibility factors of the two reference fluids expressed as functions of reduced temperature, pressure and volume. To apply the method to a mixture, therefore, it is necessary to obtain averaged critical properties by the use of mixing rules. The only difference between the LK and LKP methods lies in the value of the parameter η in the mixing rules which are defined as follows. First the critical compressibility factor for each component i is defined from the acentric factor by:

$$Z_{ci} = 0.2905 - 0.085\omega_i$$

and hence the critical molar volumes:

$$v_{ci} = Z_{ci}RT_{ci} / p_{ci}$$

The main mixing rules have the form:

$$Z_{c,mix} = \sum_i x_i Z_i$$

$$v_{c,mix} = \sum_{ij} x_i x_j \left(\frac{v_{ci}^{1/3} + v_{cj}^{1/3}}{2}\right)^3$$

$$T_{c,mix} = \frac{1}{v_c^{\eta}} \sum_{ij} x_i x_j \left(\frac{v_{ci}^{1/3} + v_{cj}^{1/3}}{2}\right)^{3\eta} \sqrt{T_{ci}T_{cj}}\,k_{ij}$$

$$p_{c,mix} = RT_{c,mix}Z_{c,mix} / v_{c,mix}$$

where T_c and p_c denote the critical pressure and temperature, k_{ij} denotes the BIP the default value of which is 1, and R denotes the gas constant. Subscript i denotes component i. For the LK method $\eta = 1$, whereas for the LKP method $\eta = 0.25$.

In Multiflash, all the BIPs for the LK method are set to the default value of 1. For the LKP method, it is quite important to adjust the BIPs in order to get reasonable phase equilibrium predictions. Multiflash uses correlations for the BIPs proposed by Knapp et al. In these correlations the BIPs are all set to constant values, although Multiflash allows the user to use temperature dependent BIPs if required. A complete description of the method can be found in *Vapor-Liquid Equilibria for Mixtures of Low Boiling Point Substances* by Knapp, Döring, Oellrich, Plöcker and Prausnitz, Chemistry Data Series Volume VI, Dechema 1982.

When to use LK or LKP

The methods predict fugacity coefficients, thermal properties and volumetric properties of a mixture. However, they are rather slow and complex compared to the cubic equations of state and are not particularly recommended for phase equilibrium calculations, although they can yield accurate predictions for density and enthalpy. They would normally be applied to non-polar or mildly polar mixtures such as hydrocarbons and light gases.

Benedict-Webb-Rubin-Starling (BWRS) equation of state

The BWRS equation method is an 11 parameter non-cubic equation of state. It is described by

$$p = \frac{RT}{V}\left(N + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^5} + \frac{C'}{V^2}\left(1 + \frac{\gamma^2}{V^2}\right)\exp\left(-\frac{\gamma^2}{V^2}\right)\right)$$

where:

$$B = B_0 - \frac{1}{RT}\left(A_0 + \frac{C_0}{T^2} - \frac{D_0}{T^3} + \frac{E_0}{T^4}\right)$$

$$C = b^3 - \frac{1}{RT}\left(a^3 + \frac{d^3}{T}\right)$$

$$D = \frac{\alpha^3}{RT}\left(a^3 + \frac{d^3}{T}\right)$$

$$C' = \frac{c^3}{RT^3}$$

Mixing rules are used to calculate the parameters from pure component properties as follows:

$$N = \sum_i n_i$$

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

$$A_0 = \sum_{ij} \sqrt{A_{0i} A_{0j}}\left(1 - k_{ij}\right) n_i n_j$$

$$C_0 = \sum_{ij} \sqrt{C_{0i} C_{0j}}\left(1 - k_{ij}\right)^3 n_i n_j$$

$$D_0 = \sum_{ij} \sqrt{D_{0i} D_{0j}}\left(1 - k_{ij}\right)^4 n_i n_j$$

$$E_0 = \sum_{ij} \sqrt{E_{0i} E_{0j}}\left(1 - k_{ij}\right)^5 n_i n_j$$

$$b = \sum_i b_i n_i$$

$$a = \sum_i a_i n_i$$

$$c = \sum_i c_i n_i$$

$$d = \sum_i d_i n_i$$

$$\alpha = \sum_i \alpha_i n_i$$

$$\gamma = \sum_i \gamma_i n_i$$

where k_{ij} is a binary interaction parameter. For methane, ethane, ethylene, propane, propylene, isobutane, n-butane, isopentane, n-pentane, hexane, heptane, octane, carbon dioxide, hydrogen sulphide and carbon dioxide, the pure component parameters B_{0i}, A_{0i}, C_{0i}, D_{0i}, E_{0i}, b_i a_i, c_i, d_i, α_i and γ_i are set to values recommended by Starling in his book 'Fluid Thermodynamic Properties for Light Petroleum Systems', Gulf Publishing Co., Houston, 1973. For other substances the pure component parameters are estimated using correlations developed by Starling and Han which are given in the same book.

When to use the BWRS equation

The BWRS equation gives much more accurate volumetric and thermal property predictions for light gases and hydrocarbons. Given suitable interaction parameters it should give reasonable vapour-liquid phase equilibrium predictions but owing to its complexity, it requires more computing time than the cubic equations of state. The BWRS model has been superseded by the GERG-2008 model (see below) and is not recommended unless there is a specific requirement.

Multi-reference fluid corresponding states (CSMA) model

The Multiflash CSMA model is based on a collection of very accurate equations of state for a number of reference fluids. It provide accurate values of properties for any of the reference fluids (see below for a list) and uses a 1-fluid corresponding states approach to estimate mixture properties. It are formulated so that mixture properties will reduce to the (accurate) pure component values as the mixture composition approaches each of the pure component limits.

The CSMA model definition can be considered in two distinct parts: the definition of pseudo-critical properties for a mixture (mixing rules), and the prescription for combining the properties of the reference substances to give the total mixture properties (combining rules).

Mixing rules for critical properties

For the CSMA model, the mixture (pseudo) critical volume is defined as

$$V_{c,mix} = \frac{1}{N^2} \sum_{i=1} \sum_{j=1} n_i n_j V_{c,ij} l_{ij}$$

where $N = \sum_i n_i$ is the total mole number of the mixture, n_i is the mole number of component *i.* l_{ij} is a temperature-dependent binary interaction parameter for the critical volume, normally close to 1 and

$$V_{c,ij} = \frac{1}{8}\left(V_{c,i}^{1/3} + V_{c,j}^{1/3}\right)^3$$

The mixture (pseudo) critical temperature is defined as

$$T_{c,mix} = \frac{1}{N^2} \frac{\sum_{i=1} \sum_{j=1} n_i n_j T_{c,ij} V_{c,ij} k_{ij}}{V_{c,mix}}$$

where $T_{c,ij} = \sqrt{T_{c,i} T_{c,j}}$ and k_{ij} is a temperature-dependent binary interaction parameter (BIP), normally close to 1.0. This BIP has a significant effect on phase equilibrium calculations and must be fitted to match experimental data.

The mixture (pseudo) critical compressibility factor is defined as

$$Z_{c,mix} = \sum_i x_i Z_{c,i}$$

$$Z_{c,j} = \frac{P_{c,i} V_{c,i}}{R T_{c,i}}$$

The mixture (pseudo) critical pressure is then defined as

$$P_{c,mix} = \frac{Z_{c,mix} R T_{c,mix}}{V_{c,mix}}$$

BIPs for some pairs of components are stored in the INFOBIPS BIP databank. In order to improve phase equilibrium predictions, BIPs that are not available in the databank should be obtained by fitting experimental data.

The GERG-2008 mixing rules (see below) may also be used with the CSMA model combining rules and reference equations.

Combining rule for mixture thermodynamic properties

The total mixture reduced Gibbs energy is obtained by combining the pure component reduced properties as follows:

$$G_{mix}\left(T_r, P_r\right) = \sum_i x_i G_i^0\left(T_r, P_r\right)$$

where the reduced properties are defined as

$$T_r = T / T_{c,mix}$$

$$P_r = P/P_{c,mix}$$

All other thermodynamic properties are obtained from the Gibbs energy by differentiation.

Reference fluids

The current model implementation includes reference equations of state for the following substances:

acetone	fluorine	n-pentane	R13
ammonia	helium	propane	R134A
argon	heptane	propylene	R14
benzene	cyclohexane	sulphur dioxide	R141B
iso-butane	iso-hexane	SF6	R142B
n-butane	n-hexane	toluene	R143A
1-butene	hydrogen	water	R152A
iso-butene	hydrogen sulphide	xenon	R161
cis-2-butene	krypton	R11	R218
trans-2-butene	methane	R113	R22
carbon dioxide	methanol	R114	R227EA
carbon monoxide	neon	R115	R23
carbonyl sulphide	nitrogen	R116	R236EA
decane	nitrogen trifluoride	R12	R236FA
DME	nonane	R123	R245FA
dodecane	octane	R1234YF	R32
ethane	oxygen	R1234ZE	R365MFC
ethanol	iso-pentane	R124	R41
ethylene	neo-pentane	R125	RC318

The reference equations of state are taken from various sources and do not all have the same quality or range of applicability.

Any hydrocarbons that do not have reference eos are modelled by the corresponding state model published by L. Sun and J.F. Ely, International Journal of Thermoplastics, vol. 26, no. 2, p705 (2005). This model is a three-parameter model that involves two reference fluids, propane and octane, and the acentric factor of the hydrocarbons.

Applicability

The models are very accurate for pure substances that are included in the above list of reference substances. For mixtures it is necessary to fit values of the binary interaction parameters to match experimental data. in order to get the best results.

Water

A high-accuracy model for water is available as a separate model option and is also included as part of the CSMA mixture model. The reference equation of state is the IAPWS-95 formulation: *'The IAPWS Formulation 1995 for the Thermodynamic Properties of*

Ordinary Water Substance for General and Scientific Use', W. Wagner and A. Pruss, J. Phys. Chem. Ref. Data., Vol. 31, 387 (2002). The IAPWS recommended equations for transport properties have also been implemented.

Water-Ammonia

The high accuracy corresponding state model for water-ammonia binary system is based on the work developed by Beiner Tillner-Roth and Daniel G . Friend. The model not only has the high accuracy models for pure water and ammonia but also has terms for correcting the mixing behaviour. The model covers the thermodynamic space between the solid-liquid-vapour boundary and the critical locus, and is also valid in the vapour and liquid phases for pressures up to 40 MPa. It represents vapour-liquid equilibrium properties with an uncertainty of ± 0.01 in liquid and vapour mole fractions. Typical uncertainties in the single-phase regions are $\pm 0.3\%$ for the density and $\pm 200 J/mol$ for enthalpies.

Reference: Beiner Tillner-Roth and Daniel G . Friend, J. Phys. Chem. Ref. Data,Vol, 27, No. 1, 1998.

Carbon Dioxide

A high-accuracy model for carbon dioxide is available as a separate model option and is also included as part of the CSMA mixture model The equation of state is defined in: *'A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at pressures up to 800 MPa'*, R. Span and W. Wagner, J. Phys. Chem. Ref. Data., Vol. 25, 1509 (1996). The viscosity obtained from the correlation: *'The Viscosity of Carbon* Dioxide', A. Fenghour, W.A. Wakeham and V. Vesovic, J. Phys. Chem. Ref. Data., Vol. 27, 31 (1998). The thermal conductivity formulation is: *'A Reference Multiparameter Thermal Conductivity Equation for Carbon Dioxide with an Optimized Functional Form'*, G. Scalabrin, P. Marchi, F. Finezzo and R. Span, J. Phys. Chem. Ref. Data., Vol. 35, 1549 (2006).

GERG 2008 Model

The GERG-2008 EOS is an industry standard (ISO 20765-2/3) model for natural gases. It is described in the publication: O. Kunz and W. Wagner, *The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004*, J Chem. Eng. Data., **57**, 3032 (2012).

It is similar in some respects to the CSMA model described above. GERG-2008 includes accurate reference EOS for 21 natural gas components:

methane	n-pentane	argon
nitrogen	iso-pentane	oxygen
CO2	hexane	hydrogen
ethane	heptane	CO2
propane	octane	water
n-butane	nonane	helium
iso-butane	decane	H2S

The model uses different mixing rules from CSMA and additional binary departure functions that further improve the accuracy of the multi-component mixture model in the description of thermodynamic properties.

GERG-2008 Mixing rules for critical properties

The mixture (pseudo) critical volume is defined as

$$V_{c,mix} = \frac{1}{N^2}\sum_{i=1}\sum_{j=1}\frac{n_i n_j \left(n_i + n_j\right)\gamma_{ij}^{V_c} V_{c,ij}}{\beta_{ij}^{V_c} n_i + \beta_{ji}^{V_c} n_j}$$

where n_i is the mole number of component *i*, $\gamma_{ij}^{V_c}$ is a linear temperature-dependent binary interaction parameter for the critical volume, normally close to 1 and

$$V_{c,ij} = \frac{1}{8}\left(V_{c,i}^{1/3} + V_{c,j}^{1/3}\right)^3$$

The $\beta_{ij}^{V_c}$ and $\beta_{ji}^{V_c}$ are constant BIPs with values usually close to 1 and $\beta_{ij}^{V_c} = 1/\beta_{ji}^{V_c}$

The mixture (pseudo) critical temperature is defined as

$$T_{c,mix} = \frac{1}{N^2}\sum_{i=1}\sum_{j=1}\frac{n_i n_j \left(n_i + n_j\right)\gamma_{ij}^{T_c} T_{c,ij}}{\beta_{ij}^{T_c} n_i + \beta_{ji}^{T_c} n_j}$$

where $T_{c,ij} = \sqrt{T_{c,i} T_{c,j}}$ and $\gamma_{ij}^{T_c}$ is a linear temperature-dependent BIP. The $\beta_{ij}^{T_c}$ and $\beta_{ji}^{T_c}$ are constant BIPs with values usually close to 1 and $\beta_{ij}^{T_c} = 1/\beta_{ji}^{T_c}$

The BIPs for the special selected 21 natural gas components are stored in the INFOBIPS databank. If the BIPs are not available in the databank, the values are set to 1 by default.

In order to improve the phase equilibrium prediction, the BIPs that are not available in the databank for both CSM and GERG models should be obtained by fitting the experimental data.

Departure function for mixtures in GERG-2008

The Helmholtz energy reduced departure function for multi-component mixtures includes individual terms for each pure substance and binary correction terms:

$$\alpha^r\left(T_r, V_r, X\right)=\sum_{i=1} x_i \alpha_i^r+\Delta\alpha^r$$

where

$$\Delta\alpha_{ij}^r\left(T_r, V_r, X\right)=x_i x_j F_{ij} \alpha_{ij}^r\left(T_r, V_r\right)$$

The parameter F_{ij} , the weighting factor of the component, *i* and *j* in the mixture, is obtained from fitting the specific binary mixtures. The values of F_{ij} for the natural gases in the GERG-2008 model are stored in the INFOBIPS databank. If there is no departure function for a binary components, the value of F_{ij} is set to zero by default. The binary departure function, $\alpha_{ij}^r(T_r, P_r)$ is similar to the structure of a pure substance equation of state but with different equation coefficients for a typical pair of binary mixture.

Applicability

The GERG-2008 model is the recommended model for natural gases.

Activity coefficient equations in Multiflash

A number of activity coefficient equations are available in Multiflash and are described below. The nomenclature is to denote binary interaction parameters between components i and j by A_{ij}.

The NRTL equation has an additional parameter α_{ij}.

When to use activity coefficient models

Activity coefficient models are usually used to model any combination of polar and non-polar compounds including those exhibiting very strong non-ideality. If the gas phase model is the perfect gas ,the pressures should be limited to 3-5 bar. If Redlich-Kwong or another equation of state is used to model the gas phase then the pressure limit is higher, maybe of the order of 10-20 bar. However, the mixture should be subcritical. If the mixture contains some components which are above their critical point, such as dissolved gases, then you should be aware that the properties of components, e.g. vapour pressure, will be extrapolated.

NRTL, UNIQUAC and UNIFAC may be used to model VLE, LLE and VLLE but both Wilson models are limited to VLE only.

To obtain accurate predictions from any of the activity coefficient models, except UNIFAC, it is necessary to use interaction parameters. If these are not available in INFOBIPS for your system the you need to supply interaction parameters for the missing values which match the model specification given above and which are in the correct units. Parameters in INFOBIPS are in standard SI units, $Jmol^{-1}$, except for Wilson A where the BIPs are dimensionless. The user can introduce BIPs in other units provided these units are set correctly.

Ideal solution model

This is described by:

$$\frac{G^E}{RT} = 0$$

The ideal solution model may be used when the mixture is ideal, *i.e.* when there are no mixing effects. It an also be used for single components to calculate some pure component properties from the physical property databank.

Wilson equation

Wilson E equation

This is defined by:

$$\frac{G^E}{RT} = \sum_i n_i \ln\left(\frac{\sum_j G_{ij} n_j}{\sum_j n_j}\right)$$

where:

$$G_{ij} = \frac{V_j^*}{V_i^*} \exp\left(-\frac{A_{ij}}{RT}\right)$$

V_i^* is the saturated liquid molar volume of component i (extrapolated in the case of supercritical gases) evaluated at a fixed reference temperature of 298.15K.

This model may be used for vapour-liquid equilibrium calculations but it is not capable of predicting liquid-liquid immiscibility. Binary interaction parameters are provided in our INFOBIPS bank for some component pairs. If no BIPs are included for your particular mixture then to obtain accurate predictions you must supply binary interaction parameter values in the correct units.

Wilson A equation

$$\frac{G^E}{RT} = \sum_i n_i \ln\left(\frac{\sum_j A_{ij} n_j}{\sum_j n_j}\right)$$

This model which is a simplified form of the Wilson E model, may be used for vapour-liquid equilibrium calculations but it is not capable of predicting liquid-liquid immiscibility. To obtain accurate predictions you must supply binary interaction parameters (BIP) values, which are dimensionless.

NRTL equation

$$G^E = \sum_i n_i \frac{\sum_j n_j A_{ji} G_{ji}}{\sum_j n_j G_{ji}}$$

where:

$$G_{ij} = \exp\left(-\frac{a_{ij} A_{ij}}{RT}\right)$$

The NRTL model may be used for vapour-liquid, liquid-liquid and vapour-liquid-liquid calculations (the VLE option should be used for VLLE). Again if BIP values are not provided in INFOBIPS they must be supplied for accurate predictions. In cases where the user does not specify any value for the non-randomness factor, α_{ij}, it is automatically set to 0.3 if the VLE version of NRTL is specified or to 0.2 if the LLE version is specified. Note that $\alpha_{ij} = \alpha_{ji}$ so only α_{ij} need be supplied.

UNIQUAC equation

$$\frac{G^E}{RT} = \sum_i n_i \ln\left(\frac{r_i \sum_j n_j}{\sum_j r_j n_j}\right) + \frac{z}{2}\sum_i q_i n_i \ln\left(\frac{q_i \sum_j r_j n_j}{r_i \sum_j q_j n_j}\right) + \sum_i q_i n_i \ln\left(\frac{\sum_j G_{ji} q_j n_j}{\sum_j q_j n_j}\right)$$

where:

$$z = 10$$

and:

$$G_{ij} = \exp\left(-\frac{A_{ij}}{RT}\right)$$

The UNIQUAC model may be used for vapour-liquid, liquid-liquid and vapour-liquid-liquid calculations. In Multiflash we provide UNIQUAC VLE and LLE variants as for the NRTL equation. Again BIP values must be supplied for accurate predictions if they are not included in INFOBIPS. For VLLE the variant chosen should be guided by the BIPs available.

UNIFAC group-contribution methods

Original UNIFAC method

The UNIFAC method is similar to UNIQUAC but the interaction parameters are predicted based on the molecular group structure of the components in the mixture. The is completely predictive and does not require the user to supply BIPs.

$$\frac{G^E}{RT} = \sum_i n_i \ln\left(\frac{r_i \sum_j n_j}{\sum_j r_j n_j}\right) + \frac{z}{2}\sum_i q_i n_i \ln\left(\frac{q_i \sum_j r_j n_j}{r_i \sum_j q_j n_j}\right) + \frac{G}{RT} - \sum_i n_i \frac{G^{(i)}}{RT}$$

where q_i and r_i are the UNIQUAC/UNIFAC surface and volume parameters for component i and $z = 10$. For UNIFAC they are found by summing the contributions from the groups from which each component is formed. G is the residual excess Gibbs energy of the solution and $G^{(i)}$ is the residual excess Gibbs energy of

pure component i according to the principle of solution of groups. The UNIFAC residual term is given by:

$$\frac{G}{RT} = -\sum_k N_k Q_k \ln\left(\frac{\sum_l \Psi_{lk} Q_l N_l}{\sum_l Q_l N_l}\right)$$

The summation is over all groups in the mixture (or pure component). N_k is the total number of moles of group k, Q_k is the surface area parameter for group k and Ψ_{lk} is the interaction parameter:

$$\Psi_{lk} = \exp\left(-\frac{A_{lk}}{RT}\right)$$

In original UNIFAC, the two binary parameters A_{lk} between components l and k are normally taken as constants.

Dortmund modified UNIFAC method

$$\frac{G^E}{RT} = \sum_i n_i \ln\left(\frac{r_i^{3/4}\sum_j n_j}{\sum_j r_j^{3/4} n_j}\right) + \frac{z}{2}\sum_i q_i n_i \ln\left(\frac{q_i \sum_j r_j n_j}{r_i \sum_j q_j n_j}\right) + \frac{G}{RT} - \sum_i n_i \frac{G^{(i)}}{RT}$$

where q_i and r_i are the UNIQUAC/UNIFAC surface and volume parameters for component i and $z = 10$. For UNIFAC they are found by summing the contributions from the groups from which each component is formed. G is the residual excess Gibbs energy of the solution and $G^{(i)}$ is the residual excess Gibbs energy of pure component i according to the principle of solution of groups. The UNIFAC residual term is given by:

$$\frac{G}{RT} = -\sum_k N_k Q_k \ln\left(\frac{\sum_l \Psi_{lk} Q_l N_l}{\sum_l Q_l N_l}\right)$$

The summation is over all groups in the mixture (or pure component). N_k is the total number of moles of group k, Q_k is the surface area parameter for group k and Ψ_{lk} is the interaction parameter:

$$\Psi_{lk} = \exp\left(-\frac{A_{lk}}{RT}\right)$$

For Dortmund modified UNIFAC, the two binary parameters A_{lk} between components l and k are treated as quadratic functions of temperature.

Dortmund modified UNIFAC is better able to represent the simultaneous vapour-liquid equilibria, liquid-liquid equilibria and excess enthalpies of polar mixtures than the original UNIFAC

method. Like original UNIFAC, however, it does not allow for the presence of light gases in the mixture.

References: Gmehling and co-workers, *A Modified UNIFAC Model. 1. Prediction of VLE, h^E, and γ^∞*, Industrial and Engineering Chemistry Research, **26**, 1372, (1987); *A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties*, ibid., **32**, 178, (1993); *A Modified UNIFAC (Dortmund) Model. 3. Revision and Extension*, ibid., **37**, 4876, (1998); *A Modified UNIFAC (Dortmund) Model. 4. Revision and Extension*, ibid., **41**, 1678, (2002).

Regular solution theory

$$\frac{G^E}{RT} = \frac{\sum_{ij} n_i n_j V_i V_j A_{ij}}{RT \sum_i n_i V_i}$$

where:

$$A_{ij} = \frac{(\delta_i - \delta_j)^2}{2} - \delta_i \delta_j k_{ij}$$

δ_i and V_i are the solubility parameters and molar volumes at 25°C of component i.

Regular solution theory can be used for vapour-liquid calculations for mixtures of non-polar or slightly polar components. The theory is applicable to systems which exhibit negligible entropies and volumes of mixing. However, it has been largely superseded by equations of state.

Flory-Huggins theory

The Multiflash implementation of Flory-Huggins theory includes a correction term. It is defined by:

$$\frac{G^E}{RT} = \sum_i n_i \ln\left(\frac{V_i \sum_j n_j}{\sum_j n_j V_j}\right) + \frac{\sum_{ij} n_i n_j V_i V_j A_{ij}}{2RT \sum_i n_i V_i}$$

The Multiflash expression reduces to the standard Flory-Huggins theory if all interaction parameters A_{ij} are set to zero. However, to obtain reasonable results it is usually necessary to adjust the values of the interaction parameters to fit the data.

Flory-Huggins theory is able to describe systems which include some long chain molecules. It has consequently applied to model polymer systems but it has been to some extent superseded by other models such as PC-SAFT. However, Flory-Huggins theory still offers the advantages of simplicity, and hence speed.

Gas phase models for activity coefficient methods

The quantity $\ln \varphi_i^{sat}$ can be calculated from any of the gas phase models in Multiflash. The normal choices would be the perfect gas equation, the RK equation of state or a virial equation of state. The first two are described in the section on equations of state and the HOC second virial model is described below.

The Hayden-O'Connell (HOC) model

The Multiflash implementation of the HOC model treats each component in the gas phase as forming a monomer-dimer equilibrium. For most components that deviate only slightly from ideal behaviour, the model reduces to the volume-explicit virial equation:

$$V = \frac{RT}{p} + B$$

The second virial coefficient B is estimated for each component from a generalised correlation (J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem. Proc. Des. Dev, **14**, 209 (1975)). This correlation accounts for non-polar, polar and chemical association effects. The pure component properties required by the model are: critical temperature, critical pressure, radius of gyration, dipole moment and an empirical association parameter. Values for these quantities are stored in the Infodata databank.

A second virial coefficient model such as HOC can account for gas phase non-idealities up to pressures of about 5 to 10 bar. The implementation of the HOC model in Multiflash allows the vapour phase association of substances such as acetic acid to be represented.

Models for solid phases

Introduction

Multiflash may also be used to calculate the phase equilibrium of systems containing solid phases, either mixed or pure. These may occur either when a normal fluid freezes or may be a particular type of solid phase such as a hydrate.

Solid freeze-out model

This model is used to calculate the thermodynamic properties of solid phases formed by freezing one or more of the components in the fluid mixture. It may be applied to any component where this may be a consideration. The freeze-out model in general is defined by:

$$\ln \phi_i = \alpha \ln \phi_i^{liq} - \left(\frac{\Delta H - T_{ref} \Delta C_p}{R} \right) \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) + \frac{S_{corr}}{R} + \frac{\Delta C_p}{R} \ln \left(\frac{T}{T_{ref}} \right) - \frac{(p - p_{atm}) \Delta V}{RT}$$

For the freeze-out of pure solids, the parameters are as follows: φ_i is the fugacity coefficient of pure solid component i, φ_i^{liq} is the fugacity coefficient of the same component as a pure liquid at the same pressure p and temperature T (calculated from the liquid phase model associated with the freeze-out model), $\alpha = 1$, ΔH, ΔC_p and ΔV are the changes in molar enthalpy, molar heat capacity and molar volume respectively on fusion at the melting point, T_{ref} is a reference temperature which corresponds to the normal melting point when $S_{corr} = 0$ which is assumed in this case. p_{atm} is atmospheric pressure. ΔH, ΔC_p and ΔV are constants, which are normally obtained from the chosen data source.

Solid freeze-out can be used to model the solidification of compounds such as water, carbon dioxide or methane, for example in natural gases. It can also be used to model eutectics.

Scaling and general freeze-out model

In its general form, the freeze-out model can be applied to any solid phase of fixed composition, which must be defined. The

model can for example be applied to hydrated salts such as monoethylene glycol (MEG) monohydrate or to crystalline mineral salts, i.e. scales. If $\alpha = 1$, the solid fugacity coefficient is defined relative to the liquid phase of the same composition whereas, if $\alpha = 0$, the solid fugacity coefficient is an absolute value. S_{corr} is a molar enthalpy correction factor that allows the reference temperature T_{ref} to be different from the normal melting point. For solid phases that are not pure substances, the parameters ΔH, ΔC_p ΔV, S_{corr} and T_{ref} must be defined specifically for the phase in question.

Modelling hydrate formation and inhibition

Natural gas hydrates are solid ice-like compounds of water and the light components of natural gas. They form at temperatures above the ice point and are therefore a serious concern in oil and gas processing operations. The phase behaviour of systems involving hydrates can be very complex because up to seven phases must normally be considered. The behaviour is particularly complex if there is significant mutual solubility between phases, *e.g.* when inhibitors or CO_2 are present. Multiflash offers a powerful set of thermodynamic models and calculation techniques for modelling gas hydrates.

Hydrate model

The original Infochem model uses a modification of the RKS equation of state for the fluid phases plus the van der Waals and Platteeuw model for the hydrate phases. An alternative model uses the CPA model for the fluid phases. The hydrate models have also been extended to include hydrate structure H in addition to structures I and II. The model can explicitly represent all the effects of the presence of inhibitors, although parameters for the CPA model are only provided for methanol, ethanol, MEG, DEG, TEG and salt.

The main features of the models are:

- Our description of hydrate phase behaviour uses a thermodynamically consistent set of models for all phases present including hydrate structures I, II and H, ice, water, liquid and gas. The vapour pressures of pure water and sublimation pressures of ice are very accurately reproduced.
- The following natural gas hydrate formers are included: methane, ethane, propane, isobutane, butane, nitrogen, CO_2 and H_2S.
- Other hydrate formers that are not usually present in natural gas but which form structure I or II are also included. These compounds are: SF_6 , ethylene, propylene, cyclopropane, oxygen, argon, krypton and xenon.
- Parameters are provided for the following compounds that form hydrate structure II in the presence of small ‘help-gases’ such as methane or nitrogen: cyclopentane,

benzene and neopentane. These compounds and the structure H formers listed below may be present in condensate and oil systems.

- Structure H hydrates form in the presence of small 'help-gases' such as methane or nitrogen but the formation temperatures are significantly higher (about 10 K) than pure methane or nitrogen hydrate. In practice it seems that structure II hydrates form before structure H but, if there is enough water, structure H may be formed too. The structure H model includes parameters for:

  isopentane
  neohexane
  2,3-dimethylbutane
  2,2,3-trimethylbutane
  2,2-dimethylpentane
  3,3-dimethylpentane
  methylcyclopentane
  methylcyclohexane
  cis-1,2-dimethylcyclohexane
  2,3-dimethyl-1-butene
  3,3-dimethyl-1-butene
  cycloheptene
  cis-cyclooctene
  adamantane
  ethylcyclopentane
  1,1-dimethylcyclohexane
  ethylcyclohexane
  cyclohexane
  cycloheptane
  cyclooctane
- The thermal properties (enthalpies and entropies) of the hydrates and ice are included permitting isenthalpic and isentropic flashes involving these phases.
- Calculations can be made for any possible combination of phases including cases without free water. No modification of the phase models is required to do this.
- The properties of the hydrates have been fixed by investigating data for natural gas components in both simple and mixed hydrates to obtain reliable predictions of structure I, structure II and structure H hydrates.
- The properties of the empty hydrate lattices have been investigated and the most reliable values have been adopted.
- Proper allowance has been made for the solubilities of the gases in water so that the model parameters are not distorted by this effect. This is particularly important for carbon dioxide and hydrogen sulphide which are relatively soluble in water.
- Correct thermodynamic calculations of the most stable hydrate structure have been made.

The model is used to calculate the hydrate equilibrium formation temperature at a given pressure or pressure at a given temperature where the first very small quantity of hydrate appears after a sufficiently long time. This point corresponds to the

thermodynamic formation point, also known as the hydrate dissociation point. Before the thermodynamic formation point is reached hydrate *cannot* form - this point is also called the stability limit. Beyond the stability limit hydrate *can* form but may not do so for a long time.

The model has been tested on a wide selection of open literature and proprietary experimental data. In most cases the hydrate dissociation temperature is predicted to within ±1K.

Hydrates in water sub-saturated systems

Hydrates can form even in systems where there is no free water present. Our hydrate model, with both RKSAINFO and CPA used to model the fluid phase, is capable of modelling this, although the data available for validating the results are very limited. What we have noticed is that for systems with very little water and at high pressures the predicted hydrate dissociation temperatures using RKSAINFO and CPA tend to diverge with increasing pressure, with CPA predicting lower hydrate dissociation temperatures than RKSAINFO. There are no data presently available to confirm which is correct. If this causes any difficulty it is possible to reproduce the CPA predictions with RKSAINFO by using parameters which reduce the Infochem mixing rule to van der Waals. These parameters, for methane, ethane and propane with water, are stored in the file vdwbip.mfc. They can be used to overwrite the existing BIPs for these binaries by loading this file after you have defined the hydrate model based on RKSAINFO as the fluid model.

When compared to the available data all three possible variants (CPA, RKSAINFO with standard and vdw BIP) give hydrate dissociation results within experimental error.

Nucleation model

The nucleation model was developed in collaboration with BP as part of the EUCHARIS joint venture. This model is an extension of the existing thermodynamic model for hydrates described above. In order to extend the nucleation model into the Multiflash program, the following enhancements to the nucleation model were made:

- The model was extended to cover the homogeneous nucleation of ice and fitted to available ice nucleation data.
- The model was generalised to cover in principle nucleation from any liquid or gas phase.
- A correction for heterogeneous nucleation was included that was matched to available hydrate nucleation data.
- An improved expression was adopted for fluid diffusion rates.
- More robust numerical methods were introduced into the program.

The nucleation model provides an estimate of the temperature or pressure at which hydrates can be realistically expected to form. The model is based on the statistical theory of nucleation in multicomponent systems. Although there are limitations and approximations involved in this approach it has the major benefit

that a practical nucleation model can be incorporated within the framework of a traditional thermodynamic hydrate modelling package.

Many of the comparisons of model predictions with experimental data have been made. In general measurements of hydrate nucleation result in an experimental error of ± 2ºC and predictions are usually within this error band.

With the existing Infochem hydrate model and the nucleation model, the hydrate formation and dissociation boundaries can be predicted between which is the hydrate formation risk area.

Inhibitor modelling

Thermodynamic hydrate inhibitors decrease the temperature or increase the pressure at which hydrates will form from a given gas mixture. The original Infochem hydrate model includes parameters for the commonly used inhibitors: methanol, salts, and the glycols MEG, DEG and TEG and for the less well-tested inhibitors ethanol, iso-propanol, propylene glycol and glycerol. A new mixing rule was developed for the SRK equation of state to model the effects of the inhibitors on the fluid phases.

The hydrate model using CPA to model the fluid phases is limited in the current version of Multiflash to hydrate calculations with pure water or with methanol, ethanol, MEG, DEG, TEG and salt. Additional parameters to extend the CPA model to cover the full range of thermodynamic inhibitors listed above may be included in future versions.

The treatment of hydrate inhibition has the following features:

- The model can explicitly represent all the effects of inhibitors including the depression of the hydrate formation temperature, the depression of the freezing point of water, the reduction in the vapour pressure of water (*i.e.* the dehydrating effect) and the partitioning of water and inhibitor between the oil, gas and aqueous phases.
- The model has been developed using all available data for mixtures of water with methanol, ethanol, MEG, DEG and TEG. This involves representing simultaneously hydrate dissociation temperatures, depression of freezing point data and vapour-liquid equilibrium data.
- Two salt inhibition models are available. The older model is based on a salt component. The new model is a (restricted) electrolyte model. A salinity calculator tool is provided, see User Guide for Multiflash for Windows, which allows the salt composition to be entered in a variety of ways. The salt component model expresses the salt composition in terms of an equivalent "salt component" present in INFODATA with the properties of sodium chloride. The Electrolyte model in versions of Multiflash to 3.4 calculated the equivalent amount of Na+ and Cl- in the mixture. In MF3.5 the Electrolyte model has been extended to include K+ and Ca++ ions. This does not affect the equivalence calculations if the salt composition is entered as TDS (Total Dissolved Solid). If an Ion Analysis or Salt Analysis is supplied

then any values entered for K+ or Ca++ will be allocated to those ions in the Composition table and the equivalence for any ions other than Na+, K+, Ca++ or Cl- will be expressed in terms of all these four ions. The equivalent composition is based on experimental data for the freezing point depression and hydrate inhibition effect of salts.

- The solubilities of hydrocarbons and light gases in water/inhibitor mixtures have also been represented.

The original binary interaction parameters for the RKSA fluid model stored for alkanes with MEG correctly reproduce all the reported data for alkane solubility in MEG, for MEG solubility in heptane and the inhibition effect of MEG on hydrate dissociation temperatures. However, the measured data for MEG solubility in alkanes is limited to a single data set for the solubility of MEG in heptane. For mixtures containing hydrocarbons greater than C7 the parameters in versions prior to 2.9 predicted an increasing MEG solubility with increasing carbon number. This may have led to over prediction of the amount of MEG required to inhibit hydrates for heavy crude oils.

Later versions of Multiflash include new parameters for alkanes with MEG which stabilise the solubility of MEG in higher alkanes and correctly reproduce the MEG inhibition effect on hydrates. However, they fail to predict the correct solubility of alkanes in MEG. The new parameters were included in the BIP databank, oilandgas4, which is still the current version.. If, for any reason, you wish to use the original parameters you can still retrieve these from the BIP databank, oilandgas3.

Salinity Model

The original salt model operates only on a sodium chloride equivalent basis. The model represents the effect of sodium chloride in aqueous solution by a special equation of state component called “salt component” or “saltcomp”. The salt component works for all versions of RKS and PR/PR78, but it is only recommended to use it with PR, PRA, PRA-Infochem, PR78, PR78A, PR78A-Infochem, RKSA, and RKSA-Infochem. The salt component model cannot be used with the CPA model or any other equation of state.

The electrolyte salt model is designed to be added on to any equation of state. The models selection form allows it to be selected for use with the Advanced RKS equation and the CPA model. From Multiflash version 3.8 it represents the salt as a combination of sodium, potassium, calcium, chloride and bromide ions. Future versions of Multiflash may extend this to other ions

Modelling wax precipitation

Waxes are complex mixtures of solid hydrocarbons that freeze out of crude oils if the temperature is low enough. Under conditions of interest to the oil industry, waxes consist mainly of normal paraffins. Waxes are thought to consist of many crystals each of

which is a solid solution of n-paraffins of a fairly narrow range in molecular weight.

The available wax model in Multiflash is the Coutinho model. The features of the model are:

- The Coutinho model represents wax as a solid solution. There are two versions of the model, the Wilson and UNIQUAC variants. The version normally selected in Multiflash is the Wilson model which approximates the wax as a single solid solution. This approach is relatively simple to apply and gives a good representation of the data, so it is recommended for general engineering use. The more complex UNIQUAC variant models the tendency of waxes to split into several separate solid solution phases. The UNIQUAC variant can be activated by configuration files that can be supplied by Infochem for users who wish to simulate the detailed physical chemistry of wax precipitation.
- The model gives good predictions of waxing behaviour, both wax appearance temperature and the amount of wax precipitated at different temperatures. The method is applicable to both live and dead oils.
- The model requires that the normal paraffins are explicitly present in the fluid model, as these are the wax forming components. The user must therefore use the PVT Analysis either to enter the measured n-paraffin concentrations or else to estimate the n-paraffin distribution. The composition of the wax phase is determined by the known thermal properties (normal melting point, enthalpy of fusion, etc.) of the n-paraffins combined with their solution behaviour in both oil and wax phases.
- In principle the wax model can be used in conjunction with any conventional cubic equations of state. The default options in the Multiflash implementation is RKSA.

Modelling asphaltene flocculation

Asphaltenes are polar compounds that are stabilised in crude oil by the presence of resins. If the oil is diluted by light hydrocarbons, the concentration of resins goes down and a point may be reached where the asphaltene is no longer stabilised and it flocculates to form a solid deposit. Because the stabilising action of the resins works through the mechanism of polar interactions, their effect becomes weaker as the temperature rises, i.e. flocculation may occur as the temperature increases. However, as the temperature increases further the asphaltene becomes more soluble in the oil. Thus, depending on the temperature and the composition of the oil, it is possible to find cases where flocculation both increases and decreases with increasing temperature.

The asphaltene model is based on the RKS cubic equation of state with additional terms to describe the association of asphaltene molecules and their solvation by resin molecules. The interactions between asphaltenes and asphaltenes-resins are characterised by two temperature-dependent association constants: K_{AA} and K_{AR}.

The remaining components are described by the van der Waals 1-fluid mixing rule with the usual binary interaction parameters k_{ij} so the asphaltene model is completely compatible with existing engineering approaches that are adequate for describing vapour-liquid equilibria. The model is a computationally efficient way of incorporating complex chemical effects into a cubic equation of state.

Other thermodynamic models

Multiflash also incorporates a corresponding states method for estimating the density of liquid mixtures, the COSTALD model.

COSTALD liquid density model

The volume of a liquid on the saturation line is defined by:

$$\frac{V^{sat}}{V^*} = V_R^{(0)}\left[1 - \omega V_R^{(1)}\right]$$

where V^{sat} is the saturated liquid volume, V^* is a characteristic volume for each substance, ω is the acentric factor and $V_R^{(0)}$ and $V_R^{(1)}$ are generalised functions of reduced temperature. In the Infochem implementation V^* is obtained by matching the saturated liquid volume stored in the databank at 298 K or a reduced temperature of 0.7, whichever is the lower.

The volume of a compressed liquid is given by:

$$\frac{V}{V^{sat}} = \left[1 - C\ln\left(\frac{B' + p}{B' + p^{sat}}\right)\right]$$

where B' is a generalised function of reduced temperature and ω, C is a generalised function of ω, and p^{sat} is the saturation pressure at the given temperature.

The COSTALD method can provide very accurate volumes for pure substances and simple mixtures, such as LNG. It is valid for liquids on the saturation line and compressed liquids up to a reduced temperature of 0.9. It is not necessarily accurate for heavy hydrocarbon mixtures with dissolved gases.

Transport property models

Introduction

For each of the transport properties, viscosity, thermal conductivity and surface tension, Multiflash offers two approaches to obtaining values for mixtures. One route is to calculate the property for a mixture by combining the property values for the pure components of which it is composed; the mixing rule approach. The other is to use a predictive method suitable for the property in question.

Viscosity

SuperTRAPP viscosity model

The SuperTRAPP method is a predictive extended corresponding states model that uses propane as a reference fluid. It can predict the viscosity of petroleum fluids and well-defined components over a wide range of thermodynamic states from the dilute gas to the dense fluid. The basic idea behind this model is that the viscosity of a mixture can be equated to the viscosity of a hypothetical pure fluid which is then related to the viscosity of a reference fluid at a corresponding-state point (ρ_0 ,T_0). In order to improve the viscosity prediction for cycloalkanes and highly branched alkanes, the concept of mass shape factor in introduced in this method. In order to apply the method, the following are required:

- An equation of state for the reference fluid,
- Correlation for the viscosity of the reference fluid
- The critical parameters, acentric factor and molecular weight of the fluid of the interest or for each component of the mixture of the interest.

The original method is not applicable to aqueous mixtures of alcohols, glycols or salts. The Infochem implementation of Super TRAPP model includes modification to ensure that the viscosity of aqueous solutions of methanol, ethanol MEG, DEG and TEG or salts and ions are predicted reasonably well.

Two variants of the SuperTRAPP model are implemented:

- Standard Super TRAPP model as described above.

- Liquid viscosity fitting. An internal model parameter is adjusted to match the experimental measurements.

Overall the SuperTRAPP method is the most versatile method for viscosity predictions and its performance is generally better than the other methods available in Multiflash. We would recommend this method for oil and gas application. It is the default viscosity model for use with equations of state.

Reference: Huber, M. L. & Hanley, H.J.M. (1996) The corresponding-states principle: Dense Fluids. In J. Millat, J. H. Dymond & C. A. Nieto (Eds.), *Transport properties of Fluids: Their correlation, Prediction and Estimation*. Cambridge University Press.

Pedersen Model

This is a predictive corresponding states model originally developed for oil and gas systems. It is based on accurate correlations for the viscosity and density of the reference substance which is methane. The model is applicable to both gas and liquid phases. The Infochem implementation of the Pedersen model includes modifications to ensure that the viscosity of liquid water, methanol, ethanol, MEG, DEG and TEG and aqueous solutions of these components or salt are predicted reasonably well.

Reference: Pedersen, Fredenslund and Thomassen, *Properties of Oils and Natural Gases*, Gulf Publishing Co., (1989).

Pedersen Heavy Oil Model

Even though the performance of the Pedersen model in the classical form, with methane as reference component, can be stretched somewhat into the region where methane is in solid form, the classical Pedersen model is generally not suited for heavy oil mixtures with viscosities above ~10 cp.

The Pedersen heavy oil viscosity model extends the applicability area of the model for heavy oils. In this approach instead of using methane as reference component, the viscosity of the stabilised crude is used as starting point. The Ronningsen semiempirical correlation for stabilised crude viscosities is used in this model:

$$\log_{10}\eta_0 = -0.07995 - 0.1101\mathrm{M} - \frac{371.8}{T} + \frac{6.215\mathrm{M}}{T}$$

The correlation is valid at temperatures at which the fluids behave in a Newtonian manner and are not influenced by precipitated wax.

For methane reference temperature > 75 K the classical Pedersen model is used. For reference temperatures < 50 K the heavy oil model is used and for the temperature range of 50K < T < 75K the viscosity is calculated as:

$$\eta = F_1\,\eta_{Classic} + F_2\,\eta_{heavy}$$

where F1 and F2 are defined as below:

$$F_1 = \frac{HTAN + 1}{2}$$

$$F_2 = \frac{1 - HTAN}{2}$$

$$HTAN = \frac{\exp(\Delta T) - \exp(-\Delta T)}{\exp(\Delta T) + \exp(-\Delta T)}$$

With $\Delta T = \frac{T - 70}{5}$

For the temperature T in K.

By implementing the heavy oil viscosity correlation in this manner, the classical Pedersen model is still used for higher temperatures and lighter oil mixtures. Averaging the classical Pedersen model and the heavy oil correlation viscosities for methane reference temperatures in the range 50 K to 75 K ensures a smooth transition to the heavy oil viscosity correlation.

Reference: Pedersen, Fredenslund and Thomassen, *Properties of Oils and Natural Gases*, Gulf Publishing Co., (1989).

Twu Model

This is a predictive model suitable for oils. It is based on a correlation of the API nomograph for kinematic viscosity plus a mixing rule for blending oils. It is only applicable to liquids.

Reference: Twu, *Generalised method for predicting viscosities of petroleum fractions*, AIChE Journal, **32**, 2091, (1986).

Lohrenz-Bray-Clark method

This model is a predictive model which relates gas and liquid densities to a fourth degree polynomial in reduced density $\rho_r = \rho / \rho_c$:

$$\left[\left(\eta - \eta^* \right) \xi + 10^{-4} \right]^{1/4} = a_1 + a_2 \rho_r + a_3 \rho_r^2 + a_4 \rho_r^3 + a_5 \rho_r^4$$

where a_1, a_2, a_3, a_4 and a_5 are constants. For pure components the viscosity reducing parameter ξ is defined by

$$\xi = T_c^{1/6} \Big/ MW^{1/2} p_c^{2/3}$$

where T_c and p_c are respectively the critical temperature and critical pressure and MW is the component molecular weight. For a mixture these properties are calculated using mole fraction averages.

In Multiflash the fluid densities are derived from any chosen equation of state, rather than the correlations proposed by Lohrentz et al. This has the advantage that there is no discontinuity in the dense phase region when moving between liquid-like and gas-like regions.

Multiflash also allows two variants of the LBC model. The first uses the original LBC method to estimate the critical volume of petroleum fractions and takes the critical volume of other

components from the chosen data source. The second variant fits the critical volume of each component to reproduce the liquid viscosity at the boiling point.

The method is mainly applicable to the types of components found in oil and gas processing but we would recommend that the SuperTRAPP method is normally used in these cases.

Reference: Lorentz, Bray and Clark, *Calculating viscosities of Reservoir Fluids from their Compositions*, Trans. Soc. Pet. Engs. Of the AMMPE **231** 1171 (1964)

Liquid viscosity mixing rule

This method obtains the liquid mixture viscosity by applying a simple mixing rule to the pure component saturated liquid viscosities generated from a databank. Each component in the mixture must have a liquid viscosity correlation stored in the databank.

$$\ln \eta = \frac{\sum_i n_i \ln \eta_i}{\sum_i n_i}$$

Vapour viscosity mixing rule

The viscosity of a gas mixture at low density is calculated from the databank correlations for the zero pressure gas viscosities of the pure components. Each component in the mixture must have a vapour viscosity correlation stored in the databank.

$$\eta = \frac{\sum_i n_i \sqrt{M_i}\, \eta_i}{\sum_i n_i \sqrt{M_i}}$$

where M_i and η_i are the molecular weight and pure gas viscosity for component i.

Thermal conductivity

Chung-Lee-Starling thermal conductivity method

This is a predictive method for both gas and liquid mixture thermal conductivities. It requires the critical properties, T_{ci}, V_{ci} and ω_{ci} for non-polar components. For polar and associating fluids the dipole moment and an association parameter are also required. Association parameters for water, acetic acid and the lower alcohols are provided. The fluid density is required as part of the calculation and this quantity may be obtained from any of the thermodynamic models in Multiflash.

$$\lambda = \lambda_\kappa + \lambda_p$$

$$\lambda_\kappa = \lambda_0 \left[\frac{1}{H_2} + B_i Y \right]$$

where λ_0 is a generalised function of reduced temperature, B_i is a generalised function of ω, H_2 is a generalised function of ρ_r and Y is a function of volume.

This method can be used for oil and gas processing and also for polar mixtures.

Reference: Reid, Prausnitz and Poling, *The Properties of Gases and Liquids*, McGraw-Hill., (1987).

SuperTRAPP thermal conductivity method

The SuperTRAPP (STRAPP) method is an extended corresponding states model that can be used for petroleum fluids, well-defined components and pure substances.

In general the thermal conductivity is defined as the sum of the internal contribution and the translational contribution. The translational contribution can be defined as three parts: the dilute gas contribution, the residual and critical enhancement contribution. In the current version of STRAPP in Multiflash 3.9, the critical enhancement term, λ_x^{Crit} is omitted since the critical enhancement for mixtures is usually very small.

$$\lambda_x(T,\rho,\{x\}) = \lambda_x^{\text{int}}(T,\{x\}) + \lambda_x^{dilute-gas}(T,\{x\}) + \lambda_x^{res}(T,\rho,\{x\}) + \lambda_x^{Crit}(T,\rho,\{x\})$$

For a mixture, the internal contribution λ_x^{int} can be estimated from the empirical mixing and combining rules using the modified Eucken correlation for the individual components.

For the dilute gas term, the expression for the translational contribution is formulated as

$$\lambda_x^{dilute-gas}(T,\{x\}) = \frac{15R\eta_x^o(T)}{4M_x}$$

in units of *mW/m/K*. R is the molar gas constant in units of $J/mol/K$ and M_x is the molecular weight for the mixture in unit of g/mol and the expression of $\eta_x^o(T)$ for a mixture is given as follows.

$$\eta_x^o(T) = \frac{\sum_{i=1}^{n} x_i \eta_i^o(T) M_i^{1/2}}{\sum_{i=1}^{n} x_x M_i^{1/2}} \text{ and } M_x = \sum_{i=1}^{n} x_i M_i$$

Where η_i^o is the dilute gas viscosity given by Lucas correlation in unit of μP.

The expression of the residual contribution term is evaluated using the extended corresponding state method and is related to the thermal conductivity of a reference fluid of propane at a corresponding state, (ρ_o, T_o).

$$\lambda_x^{res}(T,\rho) = \lambda_o^{res}(T_o,\rho_o)F_\lambda$$

where the F_λ calculation requires mixing and combining rules for the mixtures.

References:

James F. Ely and H.J.M. Hanley , "Prediction of transport properties. 2. Thermal conductivity of pure fluids and fluid mixtures. Ind. Eng. Chem. Fund., 22, 90-97 (1983).

M.L. Huber and H.J.M. Hanley, " The Corresponding-States Principle: Dense Fluids", p283, edited by Jürgen Millet, John H. Dymond and C.A. Nieto de Castro, "Transport Properties of Fluids", IPUAC, (1996).

M.E. Baltatu, R.A. Chong, M.L. Huber, "Thermal conductivity of defined and undefined hydrocarbon liquids with an extended corresponding states model", The fourth Asian Thermophysical Properties Conference, Tokyo, Sept. 1995.

M.E. Baltatu, R.A.Chong et al, "Transport Properties of Petroleum Fractions", International Journal of Thermophyics, Vol. 20, No. 1, p85-95 (1999).

Huber(1996), p10.24, "The Properties of Gases and Liquids", edited by Bruce E. Poling, John M. Prausnitz and John P. Oconnell, fifth edition, 2001.

Liquid thermal conductivity mixing rule

This method obtains the liquid mixture thermal conductivity by applying a simple mixing rule to the pure component saturated liquid thermal conductivities generated from a databank. Each component in the mixture must have a liquid thermal conductivity correlation stored in the databank.

$$\frac{1}{\lambda^2} = \frac{\sum_i n_i M_i \frac{1}{\lambda_i^2}}{\sum_i n_i M_i}$$

where M_i and λ_i are the molecular weight and pure saturated liquid thermal conductivity of component i.

Vapour thermal conductivity mixing rule

The thermal conductivity of a gas mixture at low density is calculated from the correlations for zero density gas thermal conductivity of the pure components at the same temperature.

$$\lambda = \frac{\sum_i n_i \sqrt{M_i}\lambda_i}{\sum_i n_i \sqrt{M_i}}$$

Surface Tension

Linear Gradient Theory method

This method predicts the interfacial tension between two phases. The possible pairs of phases are: Liquid / Gas and Liquid / Liquid. The prediction of interfacial tension between Liquid / Solid and Gas / Solid phases is not yet possible.

The model uses the difference in densities between the two phases and the energy gradient that arrives from the fact that the phases are immiscible to predict the interfacial tension.

$$\sigma = \int_{\rho_I^{ref}}^{\rho_{ref}^{II}} \sqrt{2c\left(\sum_i \rho_i\left(\mu_i(\rho) - \mu_i^{eq}\right) - \left(P(\rho) - P^{eq}\right)\right)} d\rho_{ref}$$

The variable *c* is characteristic of the mixture and varies with temperature. The mixing rule used for this parameter is of the following type:

$$c_{ij} = \sqrt{c_{ii}c_{jj}}\left(1 - l_{ij}\right)$$

The parameter l_{ij} is the binary interaction parameter (BIP).

And the parameter has to be calculated along the interface gradient:

$$c = \sum_{i=1}^{Nc}\sum_{j=1}^{Nc} c_{ij}\frac{\Delta\rho_i}{\Delta\rho_{ref}}\frac{\Delta\rho_j}{\Delta\rho_{ref}}$$

As the Linear Gradient Theory model is defined in this particular way, an Equation of State that can describe the interface between the two phases is necessary. The supported Equations of State in Multiflash are SRK(A), PR(A), CPA, BWRS and SAFT.

This method has more reliable results with components present in the oil and gas processing, while using the SRK, PR or CPA Equations of State.

Reference: Zuo, Y. X. and Stenby, E. H., *A Linear Gradient Theory Model for Calculating Interfacial Tensions of Mixtures*, Journal of Colloid & Interface Science, 182 p12, Elsevier (1996)

Macleod-Sugden method

This method predicts the surface tension of a liquid mixture based on the pure component parachors stored in a databank.

$$\sigma^{1/4} = \sum P_i(\rho_l x_i - \rho_v y_i)$$

where:

P_i is the parachor for component i

ρ_l is the liquid molar density

ρ_v is the vapour molar density

x_i is the liquid mole fraction

y_i is the vapour mole fraction.

It is mainly applicable to the types of component found in oil and gas processing. There are two variants of the method: a) the 1-phase variant (MCS) where the density of the gas phase is calculated using the perfect gas equation of state. b) The 2-phase variant or advanced version (MCSA) where the properties of the gas phase are estimated using a suitable model.

Reference: Pedersen, Fredenslund and Thomassen, *Properties of Oils and Natural Gases*, Gulf Publishing Co., (1989).

Sutton

The Sutton method predicts the interfacial tension between an aqueous phase and a gas or a liquid hydrocarbon phase. The method uses the density difference between the phases and the critical pressure of the hydrocarbon phase.

$$\sigma_{hw} = \left[\frac{c_1(\rho_w - \rho_h) + c_2}{\left(\frac{T}{T_c}\right)^{a_2 + a_3 T + a_4 T^2}} \right]^{c_3}$$

where

σ_{hw} is the surface tension between water and a hydrocarbon phase

T is the temperature

T_c is the critical temperature of the hydrocarbon phase

ρ_w is the density of the aqueous phase

ρ_h is the density of the hydrocarbon phase

and

$a_1 =$	0.272727	$c_1 =$	1.53988
$a_2 =$	0.821976	$c_2 =$	2.08339
$a_3 =$	-1.83785×10^{-3}	$c_3 = 1/a_1 =$	3.66667
$a_4 =$	1.34016×10^{-6}		
$a_5 =$	302.881		

The model is mainly applicable to the type of components found in the oil and gas processing including hydrate inhibitors.

Reference: Sutton, RP, An Improved Model for Water-Hydrocarbon Surface Tension at Reservoir Conditions, SPE 124968 (2009).

Surface tension mixing rule

The surface tension for a liquid mixture may be calculated from the correlations for the surface tension of the pure saturated

liquids at the same temperature and pressure using a power law model.

$$\frac{1}{\sigma} = \frac{\sum_i n_i \frac{1}{\sigma_i}}{\sum_i n_i}$$

where σ_i is the surface tension of the pure saturated liquid for component i.

Reference: Pedersen, Fredenslund and Thomassen, *Properties of Oils and Natural Gases*, Gulf Publishing Co., (1989).

Diffusion coefficients

Fuller method

The Fuller method calculates gas diffusion coefficients. It is an empirical modification of Chapman-Enskog theory. The Fuller expression for the diffusion coefficient for components i and j in SI units is:

$$D_{ij} = \frac{1.0112 \times 10^{-22} T^{1.75} k_{ij}}{p\left(\Sigma_i^{1/3} + \Sigma_j^{1/3}\right)^2} \left(\frac{1}{M_i} + \frac{1}{M_j}\right)^{1/2}$$

T is the temperature, p is the pressure, M_i is the relative molecular weight of component i (in g mol^{-1}) and Σ_i is a characteristic volume that is found for each component using Fuller's tables. k_{ij} is an empirical adjustment factor for the user to match the Fuller method to experimental data if available; to obtain the standard result from Fuller's method, k_{ij} should be set to unity.

Reference: Chapter 11 of *The Properties of Gases and Liquids*, 5th. Ed. by Poling, Prausnitz and O'Connell, McGraw-Hill, New York, 2001.

Hayduk-Minhas method

The Hayduk-Minhas method calculates liquid diffusion coefficients. It consists of a number of empirical correlations for different classes of mixture. For example for normal paraffins the diffusion coefficient of a trace amount of component i in component j in SI units is:

$$D_{ij}^0 = \frac{7.309 \times 10^{-16} T^{1.47} \left(1000 \eta_j\right)^{\varepsilon}}{V_i^{0.71}}$$

$$\varepsilon = \frac{1.02 \times 10^{-5}}{V_i} - 0.791$$

T is the temperature, V_i is the molar volume of component i and η_j is the liquid viscosity of component j. The viscosity is calculated from the liquid viscosity model specified by the user. Details of the other correlations that form the Hayduk-Minhas method are described in the Reference. Multiflash actually returns effective diffusion coefficients for a liquid of defined composition. The expression used is:

$$D_{ij} = \left(D_{ij}^0\right)^{x_j} \left(D_{ji}^0\right)^{x_i} k_{ij}\alpha$$

$$\alpha = 1 + x_i \frac{\partial \ln \gamma_i}{\partial x_i} = 1 + x_j \frac{\partial \ln \gamma_j}{\partial x_j}$$

where x_i and γ_i are the mole fractions and activity coefficients of component i in the binary mixture. For the sake of efficiency, the activity coefficients are calculated from the Margules expression which in turn is fitted to the activity coefficients for an equimolar binary mixture calculated with the thermodynamic model for the liquid phase specified by the user. k_{ij} is an empirical adjustment factor for the user to match the calculated result to experimental data if available; to obtain the standard result, k_{ij} should be set to unity.

Reference: Chapter 11 of *The Properties of Gases and Liquids*, 5th. Ed. by Poling, Prausnitz and O'Connell, McGraw-Hill, New York, 2001.

Binary interaction parameters

Introduction

Binary interaction parameters (BIPs) are adjustable factors which are used to alter the predictions from a model until these reproduce as closely as possible the experimental data. BIPs are usually generated by fitting experimental VLE or LLE data to the model in question, with the exception of UNIFAC and PSRK BIPs which are predicted by group contribution. BIPs apply between pairs of components. However, the fitting procedure may be based on both binary and multi-component phase equilibria information, the former being the most common.

Number of BIPs related to any model

Different models require differing numbers of BIPs and these may or may not have physical significance. The cubic equations of state (RK, RKS, PR) require only a single BIP. The closer the binary system is to ideality the smaller the size of the BIP, which will be zero for ideal systems. It is unlikely that the value of the BIP will be greater than 1, although it is possible for it to be negative. For the LK and LKP models the default value of the interaction parameter is 1.

When non-standard mixing rules are used, e.g. when using RKSA(Infochem), then the number of BIPs increases. For the excess Gibbs energy type mixing rules (MHV2-type and Huron-Vidal-type) the number of BIPs will be determined by the activity coefficient model used to describe the liquid phase. For the Infochem mixing rule 3 BIPs are needed.

PC-SAFT requires two symmetric BIPs, in addition to the pure component model parameters. The default value for both is zero.

CPA uses the same interaction parameters as RKSA with the addition of three association parameters to describe cross association and self association where this occurs.

The Wilson A and UNIQUAC models require two BIPs; Wilson E needs the same number of BIPs, but these are not interchangeable with Wilson A. NRTL needs two binary energy interaction parameters and a non-randomness factor, α. With the exception of α, these BIPs may take a wide range of numerical values and more that one set may adequately represent the same experimental data. The BIPs for the activity models are asymmetric

and it is important to define the binary pair of components i and j in the correct order to agree with the fitted or reported BIPs.

The NRTL α parameter defaults to 0.3 for VLE calculations and 0.2 for LLE calculations. Values derived from fitting to experimental data will vary but are unlikely to be much greater than 0.6.

The Regular Solution and Flory Huggins models both use a BIPs that are symmetrical, dimensionless and with a default value of zero.

Units for BIPs

The BIPs for equation of state methods are dimensionless, with the exception of two of the CPA association parameters. For some of the activity coefficient models they are dimensioned with the exception of Wilson A, Regular Solution and Flory Huggins. The dimensions used in Multiflash are J/mole. If BIPs from external sources are used in Multiflash it is important that either the BIP units are changed to match the input values or the numeric values of the BIPs are changed to J/mole.

The choice of units appears once the Units button is selected in the BIP display. J/mol is the Multiflash standard for the dimensioned activity model BIPs. Cal/mol and K are the values used in the Dechema Data Series for activity VLE and LLE BIPs. The "Aspen" format allows you to transfer the BIP values for the NRTL equation produced from Aspen Plus without further change.

Temperature dependence of BIPs

In most of the open literature sources the reported binary interaction parameters will be temperature independent, *i.e.* constants. However, Multiflash allows for any BIP to be temperature dependent with either a linear or a quadratic dependence, although we do not recommend this for the NRTL α parameter. The BIPs can in general be defined as

$$A_{ij} = a_{ij} + b_{ij}T + c_{ij}T^2$$

where T is the absolute temperature in K. The user can enter the three coefficients a_{ij}, b_{ij} and c_{ij}.

Changing units

For activity coefficient BIPs, it is possible to change units. The equation above is valid for the default units of J/mol. To convert to calories the coefficients are divided by 4.18J/cal. To convert to K, the coefficients are divided by the gas constant, R = 8.31441J/mol K. To convert to the dimensionless form, the expression for A_{ij} is divided by RT and the first two terms are reordered to give

$$A_{ij}/RT = d_{ij} + e_{ij}/T + f_{ij}T$$

where

$$d_{ij} = b_{ij} / R$$
$$e_{ij} = a_{ij} / R$$
$$f_{ij} = c_{ij} / R$$

The NRTL α parameter is dimensionless so it is given by

$$\alpha_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2$$

for all units except the Aspen units when it is expressed as

$$\alpha_{ij} = d_{ij} + e_{ij} t + f_{ij} t^2$$

where t is the temperature in °C. The conversion factors are

$$d_{ij} = a_{ij} + b_{ij} \times 273.15 + c_{ij} \times 273.15^2$$
$$e_{ij} = b_{ij} + 2c_{ij} \times 273.15$$
$$f_{ij} = c_{ij}$$

BIPs available in Multiflash

Our main BIP bank is applicable to oil and gas processing operations and called appropriately, OILANDGAS. This contains BIPs for the cubic equation of state models PR, PRA, PR78, PR78A, PR-HVP, RKS, RKSA, RKS-HVP, and RKSA (Infochem) for hydrocarbons, water, methanol, glycols, H_2S, CO_2 and N_2, and for the CPA model. The correlations have been extended to include BIPs for the LKP model for hydrocarbon and light gas mixtures. Multiflash also provides methods for estimating BIPs for the PR, RKS and CPA equations for mixtures that include petroleum fractions.

The INFOBIPS BIP bank includes BIPs for the WilsonE and the VLE variants of NRTL and UNIQUAC, based on the data reported in the Dechema Chemistry Data Series. Some BIPs are also available for equations of state such as BWRS, LKP and the cubics for systems not covered by the normal correlations, e.g. binaries including ammonia. The INFOBIPS databank is updated as data are available. A BIP bank, INFOLLBIPS, stores BIPs for use with the LLE variants of NRTL and UNIQUAC.

For the UNIFAC model, BIPs are predicted from group contributions. The data records for pure components in the INFODATA databank contain information on UNIFAC groups, where applicable, enabling the BIPs to be generated. Groups for use with the PSRK and Dortmund Modified UNIFAC models are also stored as part of the pure component UNIFAC record. Where the groups vary, Multiflash applies the correct group structure to match the chosen model. We have created an Infochem version of DIPPR that includes the same group information. You will see a warning message if the group contributions are missing for any chosen component.

It is possible to have two BIP banks in force for any problem. All the .mfc model descriptions for the equations of state define both INFOBIPS and OILANDGAS. When the model is defined Multiflash will first search INFOBIPS for any specific binary BIPS, then define BIPs from the correlations in OILANDGAS and if any are still

missing they will be set to default values. The VLE variants of the activity methods only access INFOBIPS, but the LLE variants access INFOLLBIPS, followed by INFOBIPS.

Between releases of Multiflash we may amend, or add to, the BIPs stored. For the OILANDGAS databank we will supply a copy of the previous banks in order to maintain backward compatibility. The current version will still be known as OILANDGAS4, and also the default, OILANDGAS. Previous versions such as OILANDGAS3 can be recalled if you wish. For INFOBIPS we intend only to issue the latest version, if users wish to maintain access to earlier versions they should retain a copy of the relevant file.

Model data requirements

Each model requires a certain amount of pure component data. These are listed in the following table.

Model	Minimum input
Thermodynamic	
RKS	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), perfect gas Cp (CPIDEAL)
RKSAPI	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), perfect gas Cp (CPIDEAL)
RKSA	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), vapour pressure (PSAT), saturated liquid density (LDENS), perfect gas Cp (CPIDEAL)
RKSAINFO	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), vapour pressure (PSAT), saturated liquid density (LDENS), perfect gas Cp (CPIDEAL)
RKS-HVP	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), perfect gas Cp (CPIDEAL)
PR	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), perfect gas Cp (CPIDEAL)
PR78	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), perfect gas Cp (CPIDEAL)
PRA	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), vapour pressure (PSAT), saturated liquid density (LDENS), perfect gas Cp (CPIDEAL)
PR78A	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), vapour pressure (PSAT), saturated liquid density (LDENS), perfect gas Cp (CPIDEAL)
PR-HVP	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), perfect gas Cp (CPIDEAL)
PSRK	critical temperature (TCRIT), critical pressure

	(PCRIT), acentric factor (ACENTRICFACTOR), vapour pressure (PSAT), saturated liquid density (LDENS), perfect gas Cp (CPIDEAL)), UNIFAC subgroup structures (UNIFAC)
PSRK-NRTL	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), vapour pressure (PSAT), saturated liquid density (LDENS), perfect gas Cp (CPIDEAL)).
LK	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), perfect gas Cp (CPIDEAL)
LKP	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), perfect gas Cp (CPIDEAL)
BWRS	critical temperature (TCRIT), critical pressure (PCRIT), critical volume (VCRIT) and acentric factor (ACENTRICFACTOR) *for components not in model database*, perfect gas Cp (CPIDEAL)
CSMA	critical temperature (TCRIT), critical pressure (PCRIT), critical volume (VCRIT), perfect gas Cp (CPIDEAL)
CPA	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), vapour pressure (PSAT), saturated liquid density (LDENS), association parameters (ASSBE, ASSEP, ASSGA), perfect gas Cp (CPIDEAL)
ZJ	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), perfect gas Cp (CPIDEAL)
PC-SAFT	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), PC-SAFT parameters (SAFTEK, SAFTSIGMA, SAFTM, SAFTKAPPA, SAFTEPSILON, SAFTFF), perfect gas Cp (CPIDEAL). Note (1) TCRIT, PCRIT and ACENTRICFACTOR are necessary to generate starting values for flash calculations but do not affect the computed results from PC-SAFT. (2) SAFTKAPPA, SAFTEPSILON and SAFTFF are only needed for associating components.
Ideal solution	vapour pressure (PSAT), saturated liquid density (LDENS)
NRTL	vapour pressure (PSAT), saturated liquid density (LDENS)
Wilson	vapour pressure (PSAT), saturated liquid density (LDENS)
UNIQUAC	vapour pressure (PSAT), saturated liquid density (LDENS), surface and volume parameters (UNIQQ, UNIQR)
UNIFAC	vapour pressure (PSAT), saturated liquid density (LDENS), UNIFAC subgroup structures (UNIFAC)
Dortmund Modified	vapour pressure (PSAT), saturated liquid density

UNIFAC	(LDENS), UNIFAC subgroup structures (UNIFAC)
Regular Solution	vapour pressure (PSAT), saturated liquid density (LDENS), solubility parameter (SOLUPAR) and molar volume at 25°C (V25).
Flory-Huggins	vapour pressure (PSAT), saturated liquid density (LDENS), solubility parameter (SOLUPAR) and molar volume at 25°C (V25).
perfect gas	perfect gas Cp (CPIDEAL)
RK	critical temperature (TCRIT), critical pressure (PCRIT), perfect gas Cp (CPIDEAL)
Hayden O'Connell	critical temperature (TCRIT), critical pressure (PCRIT), radius of gyration (RADGYR), dipole moment (DIPOLEMOMENT), Hayden-O'Connell association parameter (HOCASS), perfect gas Cp (CPIDEAL)
Freeze-out	melting point (TMELT), enthalpy of fusion (HMELT), heat capacity change on fusion (CPMELT), volume of fusion (VMELT)
Hydrate	potential parameters (HYD1, HYD2, HYD3), cavity occupation code (HYDOC)
Wax	melting point (TMELT), enthalpy of fusion (HMELT), heat capacity change on fusion (CPMELT), volume of fusion (VMELT)
Asphaltene	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), vapour pressure (PSAT), saturated liquid density (LDENS),
Transport properties	
Pedersen	critical temperature (TCRIT), critical pressure (PCRIT), molecular weight (MOLECULARWEIGHT)
Twu	molecular weight (MOLECULARWEIGHT), boiling point (TBOIL), vapour pressure (PSAT), saturated liquid density (LDENS)
LBC Lohrenz-Bray-Clark	critical temperature (TCRIT), critical pressure (PCRIT), critical volume (VCRIT), dipole moment (DIPOLEMOMENT), molecular weight (MOLECULARWEIGHT)
CLS Chung-Lee-Starling	critical temperature (TCRIT), critical volume (VCRIT), dipole moment (DIPOLEMOMENT), molecular weight (MOLECULARWEIGHT)
STRAPP SuperTRAPP method	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), critical volume (VCRIT), dipole moment (DIPOLEMOMENT), molecular weight (MOLECULARWEIGHT)
Linear Gradient Theory	surface tension (STENSION), critical temperature (TCRIT)
Macleod-Sugden	parachor (PARACHOR)
Costald	critical temperature (TCRIT), critical pressure (PCRIT), acentric factor (ACENTRICFACTOR), saturated liquid density (LDENS)

Liquid viscosity mixing rule	liquid viscosity (LVISC)
Vapour viscosity mixing rule	vapour viscosity (VVISC)
Liquid thermal conductivity mixing rule	liquid thermal conductivity (LTHCOND)
Vapour thermal conductivity mixing rule	vapour thermal conductivity (VTHCOND)
Surface tension mixing rule	surface tension (STENSION)
Diffusivity – Fuller's method	molecular weight (MOLECULARWEIGHT), chemical formula (FORMULA), UNIFAC subgroup structures (UNIFAC).
Diffusivity - Hayduk-Minhas method	critical temperature (TCRIT), critical molar volume (VCRIT), normal boiling point (TBOIL), parachor (PARACHOR) dipole moment (DIPOLEMOMENT), saturated liquid density (LDENS), chemical formula (FORMULA), UNIFAC subgroup structures (UNIFAC).

Components

Introduction

Multiflash recognises three types of component. Normal components are pure compounds such as hydrocarbons, petrochemicals and chemicals, which may exist as gas, liquid or solid depending on conditions of temperature and pressure. A petroleum fraction is a pseudo component, usually a complex mixture of hydrocarbons, whose aggregate properties are characterised by standard tests, the results of which may be found in PVT laboratory reports.

The physical properties for each type of component are stored or defined differently.

Normal components

The physical properties of normal components are usually stored in databanks. Multiflash offers two, INFODATA and DIPPR™. INFODATA is the Infochem fluids databank, which contains data on about 200 compounds and is always supplied as part of Multiflash. DIPPR, produced under the auspices of AIChE, currently has data for over 1700 compounds, but is extended annually.

Properties of normal components

Both INFODATA and DIPPR store data for each variable property (e.g. vapour pressure, liquid density) of a component as a function of temperature. Properties that are not temperature dependent are stored as constant values. A list of the properties available in DIPPR and INFODATA is shown below. Some properties may be missing for individual components.

Constant properties

Molecular Weight
Critical Temperature
Critical Pressure
Critical Volume
Critical Compressibility Factor
Melting Point
Triple Point Temperature
Triple Point Pressure
Normal Boiling Point (at 1 atm)

Liquid Molar Volume at 298.15K
Standard perfect gas Enthalpy of Formation at 298.15K
Standard perfect gas Gibbs Energy of Formation at 298.15K
Standard perfect gas Entropy at 298.15K
Enthalpy of Fusion at Melting Point
Entropy of Fusion at Melting Point
Heat capacity change on fusion
Volume change on fusion
Standard Net Enthalpy of Combustion at 298.15K
Acentric Factor
Radius of Gyration
Parachor
Solubility Parameter at 298.15K
Dipole Moment
van der Waals Volume (UNIQUAC r)
van der Waals Area (UNIQUAC q)
Refractive Index
Flash Point
Lower Flammability Limit
Upper Flammability Limit
Autoignition Temperature

plus some model specific parameters.

Additionally there is a group of properties that allow unique identification of the name and type of the component. These are

TYPE
CAS number
FORMULA
FAMILY code

Normal databank components will be TYPE 1.

Temperature Dependent Properties

Solid Density
Liquid density
Vapour Pressure
Enthalpy of vaporisation
Solid Heat Capacity
Liquid Heat Capacity
perfect gas Heat Capacity
Second Virial Coefficient
Liquid Viscosity
Vapour Viscosity
Liquid Thermal Conductivity
Vapour Thermal Conductivity
Surface tension
Relative permittivity (dielectric constant)

Both databanks, in addition to the properties above, also contain the UNIFAC and PSRK group structures, where applicable. For some components, coefficients will also be stored for the second virial coefficient and relative permittivity, both used for model calculations.

INFODATA contains only a limited range of components, about 247, mainly suitable for oil and gas processing. Although every effort has been made to ensure that the data stored are correct we do not offer INFODATA as a quality assured databank.

DIPPR is developed under the auspices of the American Institute of Chemical Engineers. The databank contains a broad range of components including hydrocarbons, petrochemicals, chemicals and some metals. The correlations used in Multiflash are the recommended set for each property and component. Questions concerning quality codes and sources of data for the DIPPR databank should be referred to Infochem.

Each temperature dependent property may be stored by a variety of correlations

The temperature dependent properties are stored as coefficients of designated correlation equations. For each property there is a choice of correlation equations; each is assigned an equation number and it is this plus the property ID code and coefficients that is displayed through the Tools/Pure Component menu.

The correlation equations for each property are shown in the following table.

Pure component temperature-dependent properties

The form of each correlation is defined below. Property units are given in parentheses. They are fixed and are not affected by the `UNITS` or `INPUTUNITS` command.

The format require for each property correlation is

```
property_name equation_number coefficients Tmin Tmax;
```

`property_name` is one of the keywords from the following table.

`equation_number` identifies the correlation.

`coefficients` are the numerical values of the correlation coefficients. The number of coefficients required depends on the equation number.

For temperature dependent properties both databanks contain information on the upper and lower temperature limits for the correlation used for each component. Extrapolation routines are included in Multiflash so that pure component properties from either bank behave sensibly beyond the temperature limits of the stored correlation.

Keyword	Equation number	Additional information
`Cpideal`		perfect gas Cp correlation (J/mol K)
	0	data unknown; 0 coefficients
	1	Harmens method, 9 coefficients a3, a4, a5, a6, a7, a8, a9, Tmin, Tmax $C_p / R = a_3 + (a_4 - a_3)y^2(1 + (y-1)F(y))$

where $F(y) = a_6 + a_7 y + a_8 y^2 + a_9 y^3$, $y = \dfrac{T}{T + a_5}$

2 DIPPR equation 107, 7 coefficients
a3, a4, a5, a6, a7, Tmin, Tmax

$$C_p = a_3 + a_4\left(\frac{a_5 / T}{\sinh(a_5 / T)}\right)^2 + a_6\left(\frac{a_7 / T}{\cosh(a_7 / T)}\right)^2$$

5 DIPPR equation 100, 7 coefficients
a3, a4, a5, a6, a7, Tmin, Tmax

$$C_p = a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4$$

`Cpliquid` liquid Cp correlation (J/mol K)

0 data unknown, 0 coefficients

1 DIPPR equation 114, 9 coefficients
a1, a2, a3, a4, a5, a6, a7, Tmin, Tmax

$$C_p = a_1 / \tau + a_2 + a_3\tau + a_4\tau^2 + a_5\tau^3 + a_6\tau^4 + a_7\tau^5$$

where $\tau = 1 - T / T_c$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$C_p = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

`Cpsolid` solid Cp correlation (J/mol K)

0 data unknown, 0 coefficients

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$C_p = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

`psat` saturated vapour pressure (Pa)

0 data unknown, 0 coefficients

1 Wagner (form 1) 5 coefficients
a1, a2, a3, Tmin, Tmax

$$\ln p = \ln p_c + \frac{a_1\tau + a_2\tau^2 + a_3\tau^3}{T_r}$$

where $T_r = T / T_c$, $\tau = 1 - T_r$

2 Antoine equation, 9 coefficients
a1, a2, a3, a4, a5, a6, a7, Tmin, Tmax

$$\ln p = a_1 + \frac{a_2}{T + a_3} + a_4 T^{a_6} + a_5 \ln T + \frac{a_7}{T^2}$$

Note that if the third term is unused a4 should be set to 0 and a6 must be set to a positive value such as 1.0.

3 Wagner (form 2), 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$\ln p = \ln p_c + \frac{a_1\tau + a_2\tau^{\frac{3}{2}} + a_3\tau^3 + a_4\tau^6}{T_r}$$

where $T_r = T / T_c$, $\tau = 1 - T_r$

4 Wagner (form 3), 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$\ln p = \ln p_c + \frac{a_1\tau + a_2\tau^{\frac{3}{2}} + a_3\tau^{\frac{5}{2}} + a_4\tau^5}{T_r}$$

where $T_r = T / T_c$, $\tau = 1 - T_r$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$p = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

7 IAPWS equation

$$\ln p = \ln p_c + \left(a_1\tau + a_2\tau^{\frac{3}{2}} + a_3\tau^3 + a_4\tau^{\frac{7}{2}} + a_5\tau^4 + a_6\tau^{\frac{15}{2}}\right)/T_r$$

where $T_r = T / T_c$, $\tau = 1 - T_r$

$$T > T_c : \ln p = \ln p_c + \left(a_1\tau\right)/T_r$$

$$T < T_{\min} : \ln p = \ln p_c + \left(b_1 + b_2/T_r\right)$$

hvap enthalpy of vaporisation correlation (J/mol)

0 data unknown, 0 coefficients

1 Watson/DIPPR 106 equation, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\Delta H = a_1\tau^Y$$

where $Y = a_2 + a_3 T_r + a_4 T_r^2 + a_5 T_r^3$, $T_r = T / T_c$,
$T_r = T / T_c$, $\tau = 1 - T_r$

2 Wagner type equation for enthalpy of vaporisation, 9 coefficients
a1, a2, a3, a4, a5, a6, a7, Tmin, Tmax

$$\Delta H / RT_c = a_1\tau^{1/3} + a_2\tau^{2/3} + a_3\tau + a_4\tau^{4/3} + a_5\tau^{5/3} + a_6\tau^2 + a_7\tau^6$$

where $\tau = 1 - T / T_c$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\Delta H = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

ldens saturated liquid density correlation (mol/m3)

0 data unknown, 0 coefficients

1 Infochem equation, 5 coefficients
a1, a2, a3, Tmin, Tmax

$$\rho = a_1 + a_2\tau^{a_3}$$

where $\tau = 1 - T / T_c$

2 Hankinson and Thompson equation (modified), 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$\rho = 1/V_c + a_1\tau^{\frac{1}{3}} + a_2\tau^{\frac{2}{3}} + a_3\tau + a_4\tau^{\frac{4}{3}}$$

where $\tau = 1 - T / T_c$

Note that in the above equation ρ is the *mass* density and Vc is the critical volume *per unit mass*

3 Rackett equation (modified), 5 coefficients
a1, a2, a3, Tmin, Tmax

$$1/\rho = a_1\left(a_2 + a_3\tau\right)^Y$$

where $Y = 1 + \tau^{\frac{2}{7}},\ \tau = 1 - T/T_c$

4 DIPPR equation 105, 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$1/\rho = a_2^{\ Y} / a_1$$

where $Y = 1 + \left(1 - T/a_3\right)^{a_4}$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\rho = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

7 IAPWS equation

$$\frac{\rho}{\rho_c} = 1 + a_1\tau^{\frac{1}{3}} + a_2\tau^{\frac{2}{3}} + a_3\tau^{\frac{5}{3}} + a_4\tau^{\frac{16}{3}} + a_5\tau^{\frac{43}{3}} + a_6\tau^{\frac{110}{3}}$$

Where ρ_c is the critical density and

$$\tau = 1 - T/T_c$$

$T > T_H$: hyperbolic extrapolation

$T < T_{\min}$: Linear/quadratic extrapolation

`sdens` solid density correlation (mol/m3)

0 data unknown, 0 coefficients

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\rho = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

`lthcond` liquid thermal conductivity correlation (W/m K)

0 data unknown, 0 coefficients

1 Jamieson equation, 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$\lambda = a_1\left(1 + a_2\tau^{\frac{1}{3}} + a_3\tau^{\frac{2}{3}} + a_4\tau\right)$$

where $\tau = 1 - T/T_c$

2 DIPPR equation 101, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\ln\eta = a_1 + a_2/T + a_3\ln T + a_4 T^{a_5}$$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\lambda = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

`vthcond` vapour thermal conductivity correlation (W/m K)

0 data unknown, 0 coefficients

1 DIPPR equation 102, 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$\lambda = \frac{a_1 T^{a_2}}{1 + a_3/T + a_4/T^2}$$

2 Reduced correlation, 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$\lambda = \frac{\sqrt{T_r}}{a_1 + a_2 T_r + a_3 T_r^2 + a_4 T_r^3}$$

where $T_r = T / T_c$

3 Monatomic ideal gas, 2 coefficients, Tmin, Tmax

$$\lambda = 3750 \eta_0 R / M$$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\lambda = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

`lvisc` liquid viscosity correlation (Pa s)

0 data unknown, 0 coefficients

1 Reid, Prausnitz and Poling equation 1,
4 coefficients a1, a2, Tmin, Tmax

$$\eta = a_1 T^{a_2}$$

2 DIPPR equation 101, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\ln \eta = a_1 + a_2 / T + a_3 \ln T + a_4 T^{a_5}$$

3 Reduced correlation, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\ln\left(\eta / a_5\right) = a_1 X^{\frac{1}{3}} + a_2 X^{\frac{4}{3}}$$

where $X = \frac{a_3 - a_4}{T - a_4} - 1$

4 Reid, Prausnitz and Poling equation 2/3, 6
coefficients a1, a2, a3, a4, Tmin, Tmax

$$\ln \eta = a_1 + a_2 / T + a_3 T + a_4 T^2$$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\eta = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

`vvisc` vapour viscosity correlation (Pa s)

0 data unknown, 0 coefficients

1 DIPPR equation 102, 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$\eta = \frac{a_1 T^{a_2}}{1 + a_3 / T + a_4 / T^2}$$

2 Reichenberg equation, 5 coefficients
a1, a2, a3, Tmin, Tmax

$$\eta = \frac{a_1 T_r}{\left(1 + a_2 T_r^{a_3}\left(T_r - 1\right)\right)^{\frac{1}{6}}}$$

where $T_r = T / T_c$

3 Chapman-Enskog equation, 5 coefficients
a1, a2, a3, Tmin, Tmax

$$\eta = \frac{26.69 \times 10^{-7}\left(MT\right)^{\frac{1}{2}}}{a_1^2 \Omega^{2,2}\left(T^*, a_3\right)}$$

where

$$\Omega^{2,2} = AT^{*-B} + C\exp\left(-DT^*\right) + E\exp\left(-FT^*\right) + 0.2a_3^2 / T^*$$

$T^* = T / a_2$, $A = 1.16145$, $B = 0.14874$, $C = 0.52487$, $D = 0.77320$, $E = 2.16178$, $F = 2.43787$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\eta = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

`stension` surface tension correlation (N/m)

0 data unknown, 0 coefficients

1 DIPPR equation 106, 7 coefficients
a1, a2, a3, a4, a5 Tmin, Tmax

$$\sigma = a_1\left(1 - T_r\right)^Y$$

where $Y = a_2 + a_3T_r + a_4T_r^2 + a_5T_r^3$, $T_r = T / T_c$

2 Extended Sprow and Prausnitz equation, 5 coefficients a1, a2, a3, Tmin, Tmax

$$\sigma = a_1\tau^{a_2}\left(1 + a_3\tau\right)$$

where $\tau = 1 - T / T_c$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$\sigma = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

`virialcoeff` second virial coefficient correlation (m3/mol)

0 data unknown, 0 coefficients

1 DIPPR equation 104, 7 coefficients
a1, a2, a3, a4, a5 Tmin, Tmax

$$B = a_1 + a_2\tau + a_3\tau^3 + a_4\tau^8 + a_5\tau^9$$

where $\tau = T_c / T$

5 DIPPR equation 100, 7 coefficients
a1, a2, a3, a4, a5, Tmin, Tmax

$$B = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

`dielectric` relative permittivity/dielectric constant correlation

0 data unknown, 0 coefficients

1 Maryott-Smith equation 1, 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$\varepsilon = a_1 + a_2T + a_3T^2 + a_4T^3$$

2 Maryott-Smith equation 2, 4 coefficients
a1, a2, Tmin, Tmax

$$\varepsilon = \exp\left(a_1 + a_2T\right)$$

3 Infochem equation, 6 coefficients
a1, a2, a3, a4, Tmin, Tmax

$$\varepsilon = 1 + a_1\exp\left(-a_2T - a_3T^2 - a_4T^3\right)$$

Petroleum fractions

To define a single petroleum fraction the program requires certain characteristic properties and Multiflash will then estimate the other properties needed to support the range of calculations available in the program.

The list of possible properties to support characterisation of the fraction are:

Carbon number
Molecular weight (g/mol)
Specific gravity at 60°F relative to water at 60°F
Normal boiling point
Critical temperature
Critical pressure
Pitzer's acentric factor

However, not all of these are necessary. The minimum input sets are molecular weight, molecular weight and specific gravity; molecular weight and boiling point; boiling point and specific gravity; critical temperature, critical pressure and acentric factor. Alternatively, the boiling point can be used instead of the acentric factor.

The properties that are estimated, if they have not been provided, are:

Carbon number
Molecular weight
Normal boiling point
Critical temperature
Critical pressure
Critical volume
Acentric factor
Parachor
Dipole moment
Enthalpy of formation
Standard entropy
Perfect gas Cp
Saturated liquid density
Saturated vapour pressure
Enthalpy of evaporation
Liquid viscosity

Petroleum fractions will normally be designated as TYPE 12.

Property Calculation

The order in which properties are calculated depends on the amount of input data provided. In general the following references are used as a basis for the calculations:

Molecular weight Riazi, M.R. and Al-Sahhaf, T.A., *Fluid Phase Equilibria* **117** 217-224 (1996)

Boiling point Edmister, W.C. *Pet. Refiner* **37** 154 (1958)
Brule, M.R. and Whitson, C.H., SPE Monograph 20 (2000)
Riazi, M.R. and Al-Sahhaf, T.A., *Ind. Eng. Chem. Research,* **34** 4145 (1995)

Specific gravity	Riazi, M.R. and Al-Sahhaf, T.A., *Ind. Eng. Chem. Research,* **34** 4145 (1995)
T_c, P_c, X	Kesler, M.G. and Lee, B.I., *Hydrocarbon Processing* **55**(3) 153 (1976) Brule, M.R. and Whitson, C.H., SPE Monograph 20 (2000) Riazi, M.R. and Al-Sahhaf, T.A., *Ind. Eng. Chem. Research,* **34** 4145 (1995
V_c	Riazi, M.R., Daubert, T.E., *Hydrocarbon Processing*, **59**, 115 (1980) Lira-Galeana, C., Firoozabadi, A. and Prausnitz, J.M., *AIChE J.*, **42(1)** 239 (1996)Riazi, M.R. and Al-Sahhaf, T.A., *Ind. Eng. Chem. Research,* **34** 4145 (1995)
Enthalpy of Formation and Standard Entropy	Reid, R.C., Prausnitz, J.M. and Poling, B.E.; *"The Properties of Gases and Liquids",* Gulf, Houston (1987)
Ideal C_p	Kesler, M.G. and Lee, B.I., *Hydrocarbon Processing* **55**(3) 153 (1976) and Harmens, A., *"Chemical Thermodynamics Data on Fluids and Fluid Mixtures",* IPC Science and Technology Press (1979)
Melting Point	Won, K.W., *Fluid Phase Equilibria*, **30** 265 (1986) Lira-Galeana, C., Firoozabadi, A. and Prausnitz, J.M., *AIChE J.*, **42(1)** 239 (1996)
Fusion properties	Morgan, D.L. and Kobayashi, R., *Fluid Phase Equilibria*, **63** 317 (1991) Won, K.W., *Fluid Phase Equilibria*, **30** 265 (1986) Brown, T.S., Niesen, V.G. and Erikson, D.D., *SPE 8505* (1994) Lira-Galeana, C., Firoozabadi, A. and Prausnitz, J.M., *AIChE J.*, **42(1)** 239 (1996)
Solubility Parameter	Pedersen, K.S., et al, *Energy and Fuels.* **5** 924 (1991)
Surface Tension	Quale, O.R., *Chem. Rev.*, **53** 439 (1958)
Liquid Viscosity	Orbey, H. and Sandler, S.I., *Canadian J. Che. Eng.*, **74** 437 (1993)

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