THEORY

# PROPERTY SYSTEM

DATE: December 2023

The property system is used by a number of applications (PHAST, SAFETI, NEPTUNE, Generic Spreadsheet) and models both pure component and multi-component property calculations. It makes use of the DIPPR database for pure component thermo-physical property data, and for additional flammable/toxic properties.  This report documents the latest more rigorous multi-component version (XPRP) of the property system, and highlights changes with respect to the old property version (PRP).

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| 1 | Jan 2005 | SAFETI 6.5 | P. Topalis, S. Wilkinson, H. Witlox | | |
| | | | H. Witlox | | |
| 2 | Nov 2009 | Phast 6.6 | M. Harper | | |
| 3 | April 2020 | Safeti-NL 8.3 | J. Stene | | |
| 4 | May 2021 | Apply new template | D. Vatier | | |
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# ABSTRACT

This report describes the underlying theory behind the DNV property system. This system performs a range of functions to satisfy the needs of the process models.

For thermodynamic properties, there are two distinct systems available, both of which are documented here. The older system PRP (always used by programs PHAST / SAFETI up to version 6.4) treats mixtures as behaving as a pure component typically with 'averaged' properties. More recently an alternative system XPRP (can be used by some models from programs PHAST / SAFETI 6.5) has been developed that handles multi-component mixtures in a more rigorous manner, including equilibrium calculations.

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# 1 INTRODUCTION

## 1.1 General introduction

The Property System has to perform a range of functions to satisfy the needs of the process models:

- The retrieval of pure component constant properties
- The retrieval of pure component equation coefficients for simple temperature-dependent properties, and the calculation of point property values from these coefficients
- The calculation of mixture properties from the above using mixing rules
- The calculation of thermodynamic properties of pure components and mixtures
- The solution of flash calculations

Many important properties cannot be obtained from a database, or from a simple relationship with temperature. Examples include density, enthalpy, and entropy, which are very important when predicting the behaviour of the material when it changes state (e.g. from pressure $P_1$ to pressure $P_2$ or from temperature $T_1$ to temperature $T_2$).

These properties are obtained from fundamental definitions, applied to an equation of state, and are known as "derived properties". This approach is applied to pure components (i.e. to process streams which contain a single material), and also to mixtures (i.e. to multi-component process streams).

There are currently two separate property systems: a legacy system (PRP) that was developed some years ago and has been used in many versions of **PHAST** and **SAFETI**; and a new system (XPRP) that has recently been developed and that introduces rigorous modelling of multi-component streams:

1. The older, "legacy" system (PRP) handles mixtures in a fairly simplistic manner, largely due to the fact that it does not perform flash calculations with any kind of rigour. The mixture is essentially treated as a "pseudo-component" in that its phase is determined solely by reference to a "saturated vapour pressure" that is derived using simple mixing rules on the component vapour pressures.

2. The newer system (PRP) includes rigorous modelling of multi-component phase equilibrium and thermodynamics. This new system will supersede the old system. This document described the new property system XPRP, while highlighting any differences with the old property system where applicable.

Although both systems utilise similar methods for some thermodynamic properties (e.g. equations of state for density, enthalpy and entropy calculations), the fact that the differing flash calculations will yield differing temperatures and phase compositions means that the results obtained may differ substantially.

## 1.2 Overview of property system

The structure of the property system is shown in Figure 1 below.
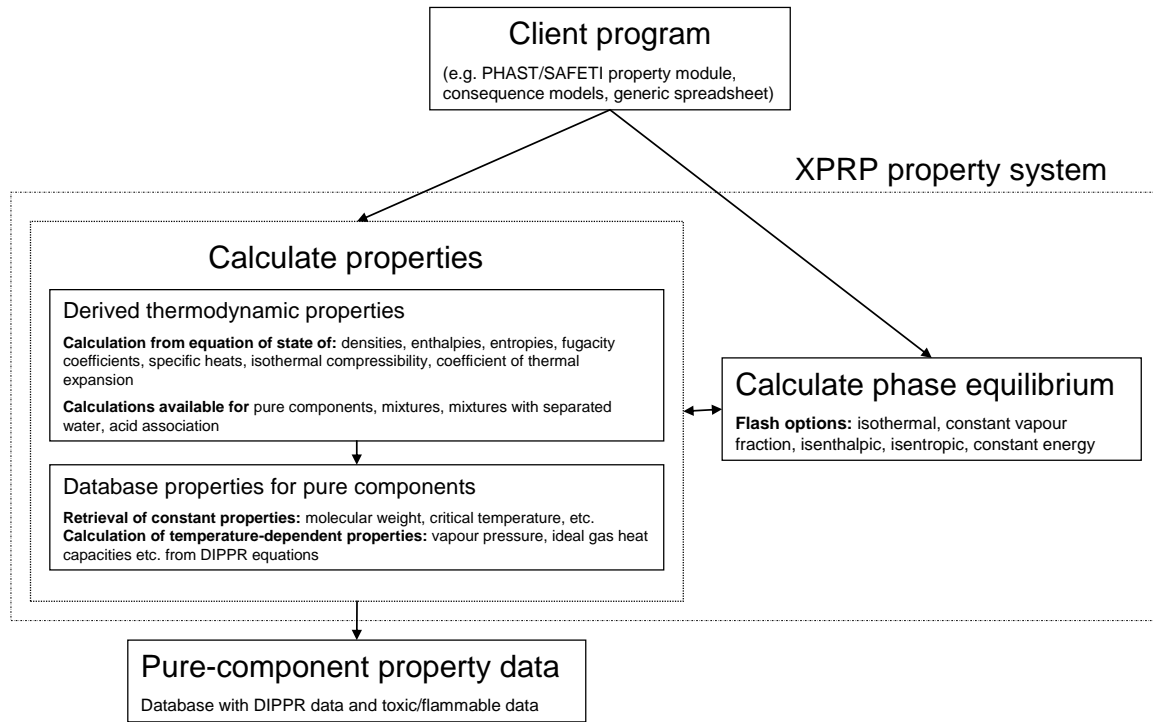


**Figure 1: The Structure of the Property System**

The property calculations can be called by any "client" programs. Currently, this includes:

1. The generic Excel spreadsheet interface for running consequence models (e.g. as used in (PHAST/SAFETI). This also includes spreadsheets for testing flash problems and mixture properties available from the flash module and the properties module.

2. The PHAST / SAFETI property module
   This program has user interface facilities for performing some flash calculations by calling the flash module, calculating multi-component and single-component properties by calling the Properties module and also updating the data files.

3. The PHAST / SAFETI Consequence Models
   The consequence models obtain property data for modelling discharge, pool vaporisation, droplet model, dispersion and scenario definition.

4. Other DNV programs such as Neptune and possibly other programs in the future

The three main calculation modules in the system are as follows:

1. <u>The phase equilibrium algorithm / flash module</u>

   This performs 2-phase (vapour-liquid) equilibrium calculations using mixture thermodynamic properties supplied by the properties module. The water phase can be treated in simplified manner as a completely separated phase. The flash module can perform five types of flash calculation:

   a. *Isothermal flash* or flash at specified temperature T and pressure P.
      This is a very useful calculation for a variety of situations. It can be used in phase identification / scenario definition before a consequence calculation. Calculation of mixed-phase stream thermodynamic properties (enthalpies, entropies) is dependent on an isothermal flash.

   b. *Constant vapour fraction flash* or flash at specified P & Vapour fraction ($\Psi$) or T & $\Psi$.
      This includes dew / bubble pressures and temperatures. This can also be very useful in phase identification /scenario identification and in a variety of consequence models.

c. *Isentropic flash* or flash at specified entropy S and pressure P.
   This is a reversible adiabatic flash and it can be used in situations usually approximated by a reversible process e.g. an orifice expansion between the bulk of the fluid and the vena contracta.

d. *Isenthalpic flash* or flash at specified enthalpy and pressure.
   This is an irreversible adiabatic flash and it can be used in processes with high degree of irreversibility e.g. the discharge through a pipe (which involves considerable friction) can be modelled with an energy balance, which, in turn, can be converted to an equivalent enthalpy balance. This is only an example where the isenthalpic flash can be a useful function for the solution of problem but it is not implied that discharge problems can generally be reduced to phase equilibrium problems.

e. *Constant Energy flash* or flash at specified energy E and pressure P.
   This flash is similar to an isenthalpic flash but the conserved quantity is not the enthalpy but the energy, i.e. the sum of the enthalpy (H) and the kinetic energy ($0.5\ u^2$). This flash has similar applications as the isenthalpic flash but it has the advantage that it avoids the assumption that the kinetic energy is negligible. The constant energy flash can be used in discharge modelling for the expansion from the stagnation point to the pipe orifice and possibly for the expansion from the pipe orifice to the atmosphere

2. The properties module for pure components

- *Retrieval of pure component constants* such as critical temperature or coefficients for the calculation of pure component temperature dependent properties from a data file. The source of the current data is the DIPPR database.

- *Calculation of pure component temperature dependent properties* such as the ideal gas enthalpy or entropy (including one pressure dependent property: saturated vapour temperature) according to the database equations

3. The properties module for derived thermodynamic properties

- *Calculation of mixture thermodynamic properties* for the purposes of the phase equilibrium module.

- *Calculation of other properties* (e.g. transport properties viscosity, thermal conductivity) using standard property mixing rules such as the ideal mixing rule or the Le Chatelier mixing rule. The mixture property interface can also be called by any other consequence model in addition to the phase equilibrium module.

The following properties are of particular interest for the phase equilibrium calculations:

- *Mixture vapour and liquid enthalpies*: $H_v$, $H_L$, used extensively in discharge and dispersion modelling

- *Mixture vapour and liquid entropies*: $S_v$, $S_L$, used especially in discharge modelling

- *Mixture vapour and liquid phase densities*: $\rho_v$, $\rho_L$, used throughout all consequence models

- *Vapour and liquid fugacity coefficients* of each component *i* in the mixture: $\phi_{v,i}$, $\phi_{L,i}$, used especially for the calculation of the equilibrium *K*-values

- *K*-values of each component *i* in the mixture:

$$K_i = \frac{(\text{component vapour mole fraction } y_i)}{(\text{component liquid mole fraction } x_i)}$$

# 1.3 Multi-component modelling in consequence analysis

A typical hazard analysis of a chemical process installation involves several hazardous materials/streams and often these streams are a mixture of two or more chemical substances. Modelling of the behaviour of the mixture requires calculation of mixture thermodynamic properties such as densities, enthalpies, entropies, fugacities and phase equilibrium conditions.

Rigorous thermodynamics is a standard feature of models used in process plant design and process simulation. However, models used in hazard and risk assessment frequently make simplistic assumptions in order to avoid the use of rigorous multi-component thermodynamics. The "pseudo component" approach is often used and the mixture is assumed to have a constant composition throughout the model and to behave like a single component. The properties of the mixture are calculated from the component properties with a simple averaging equation.

The error from a pseudo-component approach is difficult to predict but, generally, it varies according to:

- the component volatility range

- the non-ideality of the mixture

- the consequence model itself

Two-phase discharge is an example of a calculation which can be strongly affected by inaccurate thermodynamics. The actual compositions and properties of the two phases can be very different from the ones predicted from the simple pseudo-component approach, affecting the accuracy of the release flow rate calculation. TNO (1997) report a comparison between a multi-component droplet model for a mixture of ammonia-water and the equivalent single component model of Vesala and Kukkonen (1992).

The drying time of a binary droplet was a reduced by a factor of 1.5 compared to the single component ammonia droplet. A fuller discussion of MC thermodynamics as implemented in the UDM dispersion calculations can be found in Section the UDM thermodynamics model (THRM) theory and verification documentation.

A common justification of the use of simplified thermodynamics is that hazard and risk assessment do not require the same accuracy as process design. In addition to that, the integration of rigorous thermodynamics might affect the speed and robustness of the consequence models and significant investment is required to avoid these problems and keep this development under control. However, the industry often makes important decisions based on the results of consequence models and since the recent modelling technology has overcome many of the technical difficulties, this should be made available to the users of consequence models because of the resulting overall benefit: improvement of the accuracy of the risk assessment results.

# 2. PROPERTIES OF PURE COMPONENTS OBTAINED FROM DATABASE

## 2.1   Properties of pure components directly obtained from database[1]

There is a database of simple properties for pure components. Some of these properties are constant, while others are dependent on the temperature. The property system retrieves the constant properties and the coefficients of the equations describing the temperature-dependent properties, and calculates the temperature-dependent properties at the specified temperature. A complete documentation of the property database is provided in separate documentation.

Many of the constant properties and coefficients of the temperature-dependent properties have values that are taken from the DIPPR® database. A subset of these data is given in Table 1 and Table 2. The property system uses a range of DIPPR® equations to calculate many temperature-dependent properties. Each equation expresses a different relationship between a property and the temperature. See 0 for a list of DIPPR equations.

| Property | Units |
|---|---|
| Molecular Weight | kg/kmol |
| Critical Temperature | K |
| Critical Pressure | N/m2 |
| Melting Point | K |
| Normal Boiling Point | K |
| Heat Of Combustion | J/kmol |
| Flash point | K |

**Table 1: DIPPR® constant properties**

| Property | Units |
|---|---|
| Liquid Density at Atmospheric Pressure | kmol/m3 [2] |
| Saturated Vapour Pressure | N/m2 |
| Ideal Liquid Heat Capacity | J/kmol.K [2] |
| Ideal Gas Heat Capacity | J/kmol.K [2] |
| Second Virial Coefficient | ~ |
| Liquid Viscosity | N.s/m2 |
| Vapour Viscosity | N.s/m2 |
| Liquid Thermal Conductivity | W/m.K |
| Vapour Thermal Conductivity | W/m.K |
| Liquid Surface Tension | N/m |
| Ideal Gas Enthalpy | J/kmol [2, 3] |

**Table 2: DIPPR® temperature-dependent properties**

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[1] DOC. This needs further modification to include only those properties for relevance of XPRP theory

[2] The equation coefficients calculate the property on a molar basis. This may be converted to mass basis before being returned if requested.

[3] Calculated by integration of the Ideal Gas Heat Capacity equation

Table 3 includes a subset of a list of simple properties that are used in the system but are not derived from DIPPR. These mainly relate to the flammable or toxic properties of a material. Discussion of the source for these data is included in the 'Property Database' model documentation.

| Property | Units |
|---|---|
| Lower Flammable Limit | Mole Fraction |
| Upper Flammable Limit | Mole Fraction |
| Combustion Ct* | Mole Fraction |
| Combustion At* | Mole Fraction |
| Flammable/Toxic Flag | -2 =Neither (Inert), -1 =Toxic, 0 =Both, 1 =Flammable |
| ERPG 1 | Mole Fraction |
| ERPG 2 | Mole Fraction |
| ERPG 3 | Mole Fraction |
| IDLH Concentration | Mole Fraction |
| STEL Concentration | Mole Fraction |
| Toxic Property N | |
| Toxic Property A | |
| Toxic Property B | |
| Reactivity With Atmosphere | 0 =Not Strongly Reactive, 1 =Strongly Reactive, 2 =HF Only |
| Material Produced By Reaction with Atmosphere | |
| TNT Explosion Efficiency | |
| Human Response Coefficient 1 | |
| Human Response Coefficient 2 | |
| Debilitation Factor Change 1 | |
| Debilitation Factor Change 2 | |
| Flame Type (Luminous/Smoky flame) | 0 =Luminous, 1 =Smoky, 2 = general |
| Maximum Surface Emissive Power | kW/m2 |
| Emissive Power Length Scale | M |
| NFPA Flammable[4] | |
| NFPA Toxic4 | |
| NFPA Reactivity4 | |
| Dangerous Dose | Concentration in ppm time in minutes |
| Laminar burning velocity | m/s |
| Immediate ignition category | |

**Table 3: Flammable and toxic properties**

## 2.2 Combustion properties derived from database

The property system[5] currently allows the calculation of two combustion coefficients, defined by

$$Ct = \frac{moles\ of\ fuel}{moles\ of\ fuel + moles\ of\ air} = \frac{1}{1+[AIR]} \tag{1}$$

$$At = \frac{moles\ of\ fuel + moles\ of\ air}{moles\ of\ combustion\ products} = \frac{1+[AIR]]}{[PROD]} \tag{2}$$

Here complete combustion is assumed in the above calculation; [AIR] is the moles of air required per mole of material for complete combustion, and [PROD] is the moles of product produced per mole of material. The combustion coefficient Ct is the stoichiometric concentration of the combustible fuel in air, while the combustion coefficient At is the ratio of moles before reaction to the moles after reaction.

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[4] DOC. The NFPA properties are not in the property database and not used, but are defined in the property system. These properties were included with a view to future integration with ORBIT.

[5] IMPROVE. This logic is currently part of the database-generation program, but should be moved in the future to XPRP.

The air is assumed to consist of $y_{N2}^{air}$ mole fraction $N_2$ ($y_{N2}^{air} \approx 0.79$) and $y_{O2}^{air}$ mole fraction oxygen ($y_{O2}^{air} = 1 - y_{N2}^{air} \approx 0.21$)[6]. Assuming complete combustion of the fuel into combustion oxide, the reaction is as follows:

$$C_t\{fuel\} + [1-C_t]\{y_{O2}^{air} O_2 + y_{N2}^{air} N_2\} \rightarrow [A_t^{-1} - y_{N2}^{air}(1-C_t)] \{comb.\,oxide\} + [1-C_t]\{y_{N2}^{air} N_2\} \quad (3)$$
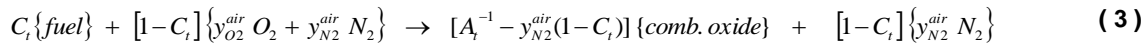
Thus $C_t$ mole of fuel reacts with $[1-C_t]$ moles of air, to form as combustion products $[A_t^{-1} - y_{N2}^{air} (1-C_t)]$ mole of combustion oxide and $y_{N2}^{air} [1-C_t]$ moles of nitrogen $N_2$.

The molecular formula of the fuel is obtained from the DIPPR database. This assumes the fuel molecule to consist of carbon (C), oxygen (O), hydrogen (H), sulphur (S), phosphorous (P), and halogens (X = bromine Br, chlorine Cl, fluorine F, and/or iodine I), Silicone (Si) and Boron (B). Thus the following reaction is assumed[7],

$$C_j H_k O_l S_m N_n P_p X_q Si_r B_s + C_1 \left[ O_2 + \frac{y_{N2}^{air}}{y_{O2}^{air}} N_2 \right] \rightarrow jCO_2 + \tfrac{1}{2}(k-q)H_2O + mSO_2 + \quad (4)$$

$$\frac{y_{N2}^{air}}{y_{O2}^{air}} C_1 N_2 + nNO + \tfrac{1}{2}pP_2O_5 + qHX + rSiO_2 + (s/2)B_2O_3$$
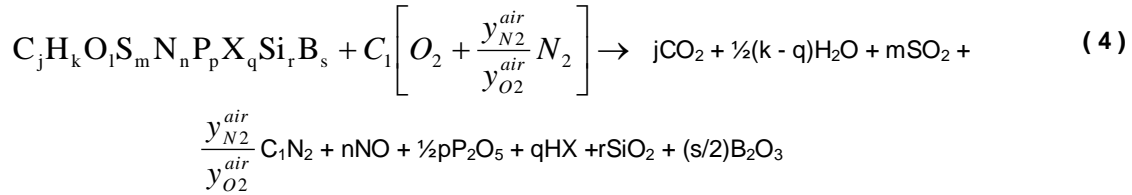
where the number of moles $C_1$ of O2 required, can be obtained by performing a stoichiometric balance on oxygen:

$$C_1 = j + \tfrac{1}{4}(k-q) + m + 5/4p - \tfrac{1}{2}l + r + \tfrac{3}{4}s + \tfrac{1}{2}n \quad (5)$$

The values of $A_T$ and $C_T$ can be obtained by:

$$A_T = [1 + (1 + \frac{y_{N2}^{air}}{y_{O2}^{air}}) 4.774C_1] / [j + \tfrac{1}{2}(k-q) + m + \frac{y_{N2}^{air}}{y_{O2}^{air}} C_1 + \tfrac{1}{2}p + q + r + \tfrac{1}{2}s + n] \quad (6)$$

$$C_T = 1 / [1 + (1 + \frac{y_{N2}^{air}}{y_{O2}^{air}}) C_1] \quad (7)$$

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[6] The code currently assumes $y_{N2}^{air} / y_{O2}^{air} = 3.774$, which corresponds to $y_{N2}^{air} \approx 0.79$

[7] This reaction assumes the conversion of the N atoms in the fuel molecule for 100% to combust to NO, and the $N_2$ present in the air to be an inert. This is in line with page 27-27 in Perry and Green (1997), which states that 95% of the fuel-bound nitrogen converts to NO. Perry indicates that the conversion of air nitrogen to NO increases with the temperature. Page 1-94 of the SFPE handbook indicates that even at 2300K the percent of conversion of N2 to NO is small (0.3).

# 3. PROPERTIES OBTAINED FROM MULTI-COMPONENT PROPERTY SYSTEM

The new property system (XPRP) has recently been developed and introduces rigorous modelling of multi-component streams. This section describes the new system. The new system also (for now) includes the properties and methods for the old system. This section describes the new property system XPRP, while highlighting any differences with the old property system PRP where applicable.

## 3.1 Overview of calculation methods for multi-component phase equilibrium

The development of calculation methods for multi-component fluid phase equilibrium has been driven largely by the process design industry. Historically, these developments followed different branches due to the diverse nature of the types of mixture needing to be modelled.

- In oil and gas processing, the components are typically hydrocarbons and other light gases (e.g. Nitrogen, Carbon Dioxide etc). Because these components are largely non-polar (or only slightly polar), and the fact that the processing frequently employs high pressures and/or temperatures, any deviations from ideal behaviour are largely associated with volumetric effects. The conventional way of modelling such systems therefore uses equations of state which attempt to model the P-V-T behaviour of the fluid.

- In the chemical industry, the components involved are often highly polar resulting in large interaction energies between molecules. The deviations from ideal behaviour are dominated by these interactions, and so the approach to modelling these systems was through the free energy or activity coefficient models.

The main advantage of the good equations of state is that they allow a uniform approach in mixture thermodynamic modelling and predict many properties for a number of possible phases (at least one vapour and one liquid phase), for multiple components and for a wide range of pressures, temperatures and compositions with a minimum number of mixture parameters. The main disadvantage is their inability to handle polar mixtures.

By contrast, activity coefficient models deal only with the liquid phase and are generally applicable within a limited range of pressure and temperatures. They can be made very accurate for even the most highly polar mixtures by using mixture interaction parameters, but are of limited value without them.

Because of the above, there has been a drive to extend the equations of state models to deal with polar mixtures through more complex mixing rules or combined free energy models.

### 3.1.1 Equation of state

The literature on equations of state is vast and it is outside the scope of this work to review these models. There are a number of text books describing the more standard and established equations (Reid et al, 1987, Walas, 1987) and a number of published paper reviews with model comparisons such as Martin (1979), Trebble and Bishnoi (1987a&b), Tsonopoulos and Heidman (1986), Vilczek and Vera (1987), Anderko (1990), Solorzano-Zavala et al (1996), Orbey and Sandler (1996). The review by Anderko (1990) is very comprehensive and covers the different types of equations.

*Cubic Equations of State*

The cubic equations of state are the most favoured by the industry for mixture calculations especially when there are very few experimental data available. Cubic equations are semi-empirical equations and they have a number of advantages:

- They are very flexible and they can easily model the fluid Pressure-Volume-Temperature (PVT) behaviour in both the liquid and the vapour phase for a wide range of temperatures, pressures and densities;

- They are quite easy to solve and there is always an analytical solution;

- They can be used to calculate simultaneously PVT properties (density), fugacity coefficients and other thermodynamic property (enthalpy, entropy, heat capacity) departures from the ideal behaviour;

- They usually have few parameters and do not require very extensive experimental data. Some of the simpler cubic equations (such as Soave(1972) and Peng Robinson(1976)) can even be used without any mixture data (or binary parameters) in some cases. Critical temperature and critical pressure data are the main requirement and most of the equations also use the acentric factor derived from vapour pressure data;

- Cubic equations usually combine easily component data to calculate mixture data;

- For mixtures, non-cubic equations are not generally more accurate than the cubic ones.

The cubic equations of state (and equations of state in general) had originally some limitations. The main limitation is the inability to cope with polar mixtures or mixtures of very dissimilar components. Research is still active in this area and some of the limitations are progressively being overcome.

*The Development of the Equations of State*

The Van der Waals (1873) equation of state was the first significant improvement over the ideal gas law and it was mainly used for PVT calculations.

The next breakthrough in this area was the Redlich-Kwong (1949) equation which was accurate enough for engineering calculations of the vapour phase fugacity coefficients but it did not model the material vapour pressure equation.

Soave (1972) modified the Redlich Kwong equation by fitting the $\alpha$-parameter of the equation to vapour pressure data using a generic (material-independent) polynomial. This modification allowed use of the equation of state for calculating fugacity coefficients for both the vapour and the liquid phase. The same equation can be used for calculating several thermodynamic properties of the vapour and liquid phase for pure materials and multi-component non-polar mixtures.

The Peng Robinson (1976) is a modification of the Soave equation presumed to improve among other things the calculation of liquid densities. The two equations are relatively simple and can be used nearly interchangeably in phase equilibrium algorithms. They are fairly accurate for modelling hydrocarbon mixtures and they can even be used without fitted binary parameters (setting $C_{ij}=1$) for mixtures of symmetric (not dissimilar) materials.

The main limitation of Soave-Redlich-Kwong (SRK) and of Peng-Robinson (PR) is modelling of medium to highly polar mixtures and also modelling of mixtures of dissimilar materials (e.g. mixtures of hydrocarbons with $H_2$ or $N_2$) materials). Use of binary interaction parameters and other small improvements to these equations, such as those implemented in our program and described in the next section, can make possible the modelling of mixtures with $H_2$, $N_2$ and other light components. However it was mainly the simplicity and universal acceptability of these 2 equations that counted in favour of their selection for this first stage of implementation of multi-component thermodynamics in our consequence models.

Since the mid-seventies, work has continued to improve the equations so that they can fit simultaneously and adequately several thermodynamic properties of the pure material: vapour pressures, vapour densities, liquid densities. Better modelling of these properties requires that the temperature dependence of the $\alpha$-parameter is improved. A number of authors including Schmidt and Wenzel (1980), Heyen (1980), Patel and Teja (1982), Adachi et al (1983), Mathias and Copeman (1983), Soave (1984), Stryjek and Vera (1986), Melhem et al(1989), Sugie et al(1989), Yu and Lu (1987) proposed various modifications of the temperature dependency of the $\alpha$-parameter, which aimed to improve the vapour pressure representation in general or for specific components ($H_2$). Other modifications of the form of the equation aimed to improve the consistency of representation of liquid densities and the critical compressibility factor e.g. Harmens and Knapp (1980), Peneloux (1982), Trebble an Bishnoi (1987a&b)

Work has also continued to improve the modelling of polar mixtures, which is described in more detail below.

## 3.1.2  Activity coefficient models

The most commonly used activity coefficient models are:

- The Wilson Equation ( Wilson (1964) ) – Utilises two adjustable interaction parameters for each binary pair in the mixture, and also uses the partial liquid molar volumes.

- The Non-Random-Two-Liquid Equation (NRTL) (Renon and Prausnitz 1968) – Utilises three adjustable interaction parameters for each binary pair in the mixture, although one of the parameters (the 'alpha' parameter) is sometimes fixed at a pre-defined value.

- The Unified Quasi-Chemical Equation (UNIQUAC) – Utilises two adjustable interaction parameters for each binary pair in the mixture, and also uses pure component parameters representing the Van der Waals volume and surface area.

Of the three models, Wilson is the only one that is incapable of describing liquid-liquid phase equilibrium. Other than this, the choice of model seems frequently to be driven by user preference, or by the availability of suitable interaction parameters.

In the absence of interaction parameters, the models effectively revert to ideal (Raoult's Law) behaviour. There is therefore a high data requirement, although this can be mitigated to a degree by using a standard compilation such as the Dechema Chemistry Data Series (University of Dortmund).

Fredenslund et al. (Technical University of Denmark) produced the UNIFAC Equation (Unified Functional Group Activity Coefficient) in order to reduce this data load. This utilises the same equation form as UNIQUAC, but the compositions and parameters are expressed in terms of Functional Groups (e.g. $-CH_2$ ,

-C=0 ). The published interaction parameters between the functional groups have been determined by regression of a huge volume of data on a wide range of mixtures in order that they can be used in a predictive way for other substances.

## 3.1.3 Approaches to modelling of polar mixtures using equations of state

The effort in this area has focused mainly on the improvement of mixing rules. The standard SRK and PR equations use the classical Van der Waals mixing rules, which are typically enhanced to include one binary interaction parameter, but the Van der Waals mixing rules appear to be inadequate for the modelling of polar mixtures. Three other types of mixing rules for cubic equations of state have been investigated during the last few years:

1. Rules based on Excess Gibbs Free Energy $G_E$ models

   These are equivalent to activity coefficient models. The most widely used $G_E$ model is NRTL (Non-Random-Two-Liquid, Renon and Prausnitz, 1968) but other models such as Wilson (1964) are commonly used.

   The first and best known $G_E$-based mixing rule was proposed by Huron and Vidal (1979).

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{g_\infty^E}{L} \tag{8}$$

   where:

   $a$ and $b$      are the cubic equation parameters

   $g_\infty^E$      is an Excess Gibbs energy function

   $L$      is a constant.

   Other authors such as Soave (1984), Kurihara et al (1987), Mollerup (1986), Gupte (1986), Heidemann and Kokal (1990), Boukouvalas et al(1994) developed further the ideas of $G_E$- based mixing rules. Wong and Sandler (1992) proposed a more sophisticated rule producing improved overall results (Solorzano-Zavala et al, 1996).

   Typically the $G_E$-based rules require 2-3 binary parameters, although some of the models can use existing activity coefficient parameters derived over a limited temperature range. The MHV2 (Modified Huron Vidal 2nd Order) equation (Michelsen) can be used with any of the liquid phase activity coefficient models (Wilson, NRTL, etc.) and has been shown to dramatically improve the prediction of high pressure vapour-liquid equilibrium results from interaction parameters derived at atmospheric pressure.

   The main advantages of these mixing rules are that they can model polar mixtures and combine the flexibility of the activity coefficient models (in terms of fitting experimental phase equilibrium data) and the wide temperature and pressure range of validity of the cubic equations of state. The disadvantages are that the $G_E$ rules require more computing time than the simple mixing rules, they predict incorrect composition dependence of the Virial coefficients and they retain some other weaknesses of the activity coefficient models (non-unique adjustable parameters) and sometimes they predict an incorrect phase split.

2. Simple composition-dependent mixing rules
   The most well-known mixing rule is the one by Panagiotopoulos and Reid (1986), where the mixture $a$ -parameter of the equation of state is represented by a simple function of the mole fractions:

$$a = \sum \sum x_i x_j \sqrt{a_i a_j} [1 - k_{ij} + x_i (k_{ij} - k_{ji})] \tag{9}$$

   This rule has 2 binary parameters.

   Stryjek and Vera (1986) and Melhem (1979) have proposed similar mixing rules. Kabadi and Danner (1985) proposed a composition-dependent mixing rule designed for hydrocarbon–water mixtures.

   The simple composition-dependent mixing rules are as flexible as the $G_E$-based rules and they are simple to use. They have the same weaknesses as the $G_E$-based rules and they may be less accurate than the $G_E$-rules for highly non-ideal systems. Michelsen and Kistenmacher (1990) have highlighted some internal inconsistencies of some of these rules: lack of invariance (results change in case of material sub-division to pseudo-components) and the "dilution effect" (anomaly due to the fact that the calculation involves multiplication of 3 mole fractions, i.e. cubed mole

fraction). Nevertheless, these rules have been relatively popular for modelling polar mixtures because of their simplicity.

3.  Density dependent mixing rules

    These rules were invented to allow a thermodynamically consistent representation of the low and high-density regions. These rules typically require 2-3 temperature dependent parameters. The rules by Mollerup (1981), Whiting and Prausnitz (1982), Luedecke and Prausnitz (1985) and Wilczel-Vera and Vera (1987) are examples of this rule category. These rules allow a small improvement over the classical mixing rules but they introduce an additional complexity and there are doubts if this is worthwhile.

## 3.1.4  Summary

There are various possibilities of further expansion of the capabilities of the thermodynamic model options in our program. However at this first stage, the SRK and PR equations allow a reasonable modelling of non-polar and slightly polar mixtures for consequence analysis purposes.

In the near future, for handling strongly polar mixtures at low to moderate pressures, the NRTL/Wilson/UNIQUAC equations should be implemented because of the relative abundance of interaction parameter data in the literature.

Longer term, if there is a strong demand for equations of state for polar mixtures in the consequence analysis area, a simple composition-dependent mixing rule such as the one by Panagiotopoulos and Reid (1986) or the MHV2 method should be considered.

## 3.2 Calculating simple properties for a mixture

When modelling a mixture, the program calculates the values of these simple properties as a composition-based average of the base properties of the individual components. A number of choices for the averaging method, or mixing rule, are available. For constant properties, the mixing rules are applied directly to the property values. For temperature-dependent properties, the mixing rules are applied to the values obtained from the equation for each of the components in the mixture at the specified temperature.

### 3.2.1 Available mixing rules

General purpose rules

Mixture properties are calculated according to mixing rules which combine the properties of each of the individual components. The rules are empirical and the program allows you to choose between them to obtain the best possible prediction of mixture properties.

Ideal mixing rules take no account of the interaction between the components. Non-ideal mixing rules take account of the attractions or repulsions between pairs of components expressed by binary interaction coefficients. Three are two forms of rule for ideal mixing (ideal and Le Chatelier) and one form of non-ideal mixing: non-ideal. The equations used in each rule are given in
Table 4[8]:

| Ideal Mixing | Le Chatelier's Mixing Rule | Non-ideal Mixing |
|:---:|:---:|:---:|
| $Q_m = \sum_{i=1}^{i=N} y_i Q_i$ | $\dfrac{1}{Q_m} = \sum_{i=1}^{i=N} \dfrac{y_i}{Q_i}$ | $Q_m = \sum_{j=1}^{j=N} \sum_{i=1}^{i=N} y_i\, y_j\, c_{ij}\, Q_i$ |

where:

| | |
|---|---|
| $Q_i$ | is the pure component property value (at the specified temperature if relevant) |
| $Q_m$ | is the mixture property value |
| $y_i$ | is the mass or mole fraction |
| $c_{ij}$ | is the binary interaction coefficient |
| $N$ | is the number of components in mixture |

**Table 4: Mixing rules for simple properties**

Max and min values
Some properties are 'mixed' by simply taking the maximum or minimum value from the individual component values.

Luminous smoky flame method
The component value of this property is either less than or equal to zero (luminous) or greater than zero (smoky). The mixing rule sums the masses of luminous and smoky components in the mixture and returns 1.0 if the smoky components are heavier and 0.0 if the luminous components are heavier. However if any of the components is of flame type 'general', then so will be the mixture.

Flammable/Toxic flag mixing
To determine whether a mixture is flammable, toxic, both or neither the component Flammable/Toxic flags are first 'mixed' as shown in the following table to give a preliminary value:

---

[8]Non-ideal mixing is not supported in the new property system. In the old property system there is in fact a single set of binary interaction coefficients for a mixture, and these appear to have been used in different contexts – for these simple properties and in equation of state methods for thermodynamic properties. However, by default no properties used non-ideal mixing and therefore these would have not been used.

| Component values | Mixture result |
|---|---|
| No toxic, no flammable, no both (only inert) | Inert (-2) |
| No toxic, no both, some flammable | Flammable(1) |
| No flammable, no both, some toxic | Toxic(-1) |
| Either at least one both or flammable and toxic components both present | Both (0) |

**Table 6. Mixing rule for the flammable/toxic flag**

If the mixture is found to be Flammable (or both) according to this preliminary determination, then the Lower Flammable Limit (LFL) is calculated from the LFLs of the flammable components using Le Chatelier's mixing rule. If the resulting LFL is greater than 1.0 mole fraction, this indicates that the concentration of the flammable components is too small for the mixture to be flammable once further diluted with air, so the result is modified to make the mixture value non-flammable.

Viscosity mixing rules
For liquid and vapour viscosity two special mixing rules are applied, Kendall-Monroe for Liquid, and Kouzel for Vapour. These are formulated as follows[9]:

**Kendall-Monroe**

$$\mu = \left[ \sum_{i=1}^{i=N} y_i \sqrt[3]{\mu_i} \right]^3$$

**Kouzel**

$$\mu = \frac{\sum_{i=1}^{i=N} \left[ y_i \mu_i \sqrt{M_{wi}} \right]}{\sum_{i=1}^{i=N} \left[ y_i \sqrt{M_{wi}} \right]}$$

where:

$\mu_i$      is the pure component viscosity (at the specified temperature if relevant)
$\mu$      is the mixture viscosity
$y_i$      is the mass or mole fraction
$N$      is the number of components in mixture
$M_{wi}$      is the component molecular weight

**Table 5: Mixing rules for viscosity**

Mixing rules for combustion coefficients
Equations ( 1 ) and ( 2 ) can be rearranged and combined to give:

$$[AIR] = \frac{1}{Ct} - 1 \tag{10}$$

$$[PROD] = \frac{1}{CtAt} \tag{11}$$

Therefore, for a mixture of N components:

$$[AIR]_{mix} = \sum_{i=1}^{N} y_i [AIR]_i = \sum_{i=1}^{n} \frac{y_i}{Ct_i} - 1 \tag{12}$$

$$[PROD]_{mix} = \sum_{i=1}^{N} y_i [PROD]_i = \sum_{i=1}^{N} \frac{y_i}{Ct_i At_i} \tag{13}$$

Substituting these back into Equations ( 1 ) and ( 2 ), yields:

---

[9] In the old property system, viscosity could not be calculated for a mixture.

$$Ct_{mix} = \frac{1}{\displaystyle\sum_{i-1}^{n} \frac{x_i}{Ct_i}}$$

( 14 )

$$At_{mix} = \frac{\displaystyle\sum_{i-1}^{n} \frac{x_i}{Ct_i}}{\displaystyle\sum_{i-1}^{n} \frac{x_i}{Ct_i At_i}}$$

( 15 )

Thus Le Chatelier's mixing rule can be used for $C_t$ while a separate rule must be used for At.

For a non-combustible components no air is required ( [AIR] = 0 ) and there is no change in moles during combustion( [PROD] = 1 ). Therefore, from Equations ( 1 ) and ( 2 ), $Ct_i = 1$ and $At_i = 1$.

Flash point

This mixing rule uses the minimum of component flash points[10]. If flash point is unset for a flammable component, it is calculated from the normal boiling point ($B_{pt,i}$) [11]:

$$F_i = 0.70497 B_{pt,i} + 18.2648$$

( 16 )

Immediate ignition category
The maximum of component values (low, medium or high) is used. Where a flammable component has no category specified, it is assumed to be 'high' for the purposes of the mixture calculation.

Laminar burning velocity
Calculated for mixtures as follows:

$$V_{mix} = \frac{\displaystyle\sum_{i=1}^{n} y_i}{\displaystyle\sum_{i-1}^{n} \frac{y_i}{V_i}}$$

( 17 )

Where

| | | |
|---|---|---|
| $y_i$ | = | Mole fraction of flammable component (*i*) (non-flammables are ignored) |
| $V_i$ | = | Laminar burning velocity of flammable component (*i*) [m/s] |
| $n$ | = | Total number of components in the mixture |

---

[10] IMPROVE A better method (suggested by Stuart Wilkinson) may be to assume the vapour will ignite once the concentration in the vapour space reaches the LFL, and that the mixture and air are in equilibrium. Then the mixture flash point will be T such that LFL×P = $\Sigma y_i P_{sat,i}$

[11] A strong correlation exists between DIPPR flash points and normal boiling points exists with a straight line fit as given in the equation.

ERPG / NLIV

There are three mixing rules available for mixture ERPG values (ERPG1, ERPG2 and ERPG3). These also apply to the Dutch equivalents, the Netherlands Intervention (NLIV) values (VRW, AGW and LBW). The three mixing rules are as follows:

- "DNV":

$$ERPG_{mix} = \min\{1, \min_{i=1,..,N;y_i>0} \frac{ERPG_i}{y_i}\} \qquad (\,18\,)$$

- "mole Le Chatelier":

$$\frac{1}{ERPG_{mix}} = \sum_{i=1}^{N} \frac{y_i}{ERPG_i} \qquad (\,19\,)$$

- "min toxic component value":

$$ERPG_{mix} = \min_{i=1,..,N} ERPG_i \qquad (\,20\,)$$

Here $ERPG_i$ and $ERPG_{mix}$ is the ERPG value of mixture component $i$ and the mixture ERPG value in unit fraction, respectively. Further $y_i$ is the mole fraction of component $i$ in the mixture. Note that all three mixing rules only include component $i$ in the calculations if all of the below holds true:

- Component $i$ is toxic.
- The composition contribution of component $i$ is positive; $y_i > 0$.
- The ERPG value of component $i$ is positive; $ERPG_i > 0$.

## 3.2.2 Default mixing rules for a new mixture

The choice of mixing-rules for the property calculation is not set globally for all of the mixtures in the database, or even for all of the properties for a given mixture. The new property system contains 'template' sets of methods for calculating properties, which use particular mixing rules for particular properties. The mixing rule should account for the phase (liquid or vapour) and may use fractions on a mass or a mole base.

Some properties rather than have a mixing rule, have a 'constant' method, in which case the property cannot be calculated, but must have a value set by a user. This is used in general for one of two reasons:

- To indicate that there is no 'recommended' method for calculating a property for a mixture, and users must be responsible for providing values.

- To replicate the old property system, where some properties were calculated only once (usually during mixture creation) and simply retrieved later[12].

Normally in these circumstances a method is provided but only invoked in Phast when the 'Calculate' button for a mixture is pressed. The calculated value is then stored as a constant, and does not change with mixture composition unless the 'Calculate' button is re-pressed.

The standard PHAST / SAFETI templates conform to the mixing rules applied in the old property system PRP. See Appendix A for further details on application of methods and templates in the new property system XPRP.

---

[12] These 'constant' properties were a limitation of SAFETI 6.4, but were a logical implementation of the pseudo-component approach, where composition was assumed fixed once the material had been created. For molecular weight ideal mixing has been applied in SAFETI 6.5 even though it was a constant property in the old system.

## 3.3 Equations of state

The equations are based on the equations for a pure material modified by means of mixing rules to apply to vapour mixtures or to liquid mixtures. There is the choice of Ideal, the Virial Equation and three cubic equations of state: Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson. These equations were chosen because they can predict the behaviour of fluids over a wide range of conditions, covering the vapour phase and the liquid phase, and covering multi-component fluids. The choice of equations of state is discussed in detail in Section 3.1.

### 3.3.1 Ideal Equation

The ideal gas is modelled by the unmodified ideal gas equation:

$$Z = \frac{PV}{RT} = 1.0$$

( 21 )

Where

| | |
|---|---|
| $Z$ | is the compressibility (-) |
| $P$ | is the absolute pressure (N/m$^2$) |
| $T$ | is the absolute temperature (K) |
| $V$ | is the molar volume (m$^3$/kmol) |
| $R$ | is the gas constant (J/kmol.K) |

So the compressibility, $Z$, is always 1.0 for an ideal gas.

### 3.3.2 Virial Equation

The virial equation itself is an expansion of the compressibility in either 1/V or P. In terms of 1/V it is as follows:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + ...$$

( 22 )

In the property system we adopt the first order virial equation, obtained by ending the expansion with the second coefficient B:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V}$$

( 23 )

Here B is the second virial coefficient. For pure components this is evaluated as a function of temperature T using its DIPPR® equation. For mixtures the ideal mixing rule is applied to the pure component values on a molar basis.

Quadratic equation of state for compressibility Z
The Virial equation is only applicable to the vapour phase. The above equation can be solved as a quadratic for $V$ once $B$, $P$ and $T$ are known.

If we do that, rearrange with the compressibility Z as the subject of the equation and eliminate V, we obtain a quadratic in Z:

$$Z^2 - Z - \frac{BP}{RT} = 0$$

( 24 )

The solution to this is:

$$Z = \frac{1 \pm \sqrt{\frac{4BP}{RT} + 1}}{2}$$

( 25 )

The maximum root is the vapour compressibility. Note that there is no real solution for the compressibility when the contents of the square root are negative i.e.

$$\frac{4BP}{RT} < -1 \qquad\qquad (\ 26\ )$$

At this point the equation fails and the property system returns an error. This reflects the fact that as we have ignored higher order terms, behaviour at high pressures is not well represented. In such circumstances one of the cubic equations of state should be used.

### 3.3.3  Three cubic equations

The three cubic equations of state employed by the property system are Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK), and Peng-Robinson (PR). These can all be written in a generalised form of the cubic equation of state as:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)+ub(V-b)} \qquad\qquad (\ 27\ )$$

For mixtures, the parameters of the equation are determined according to mixing rules:

$$a\alpha = \sum_{i=1}^{N}\sum_{j=1}^{N} y_i y_j (a_i \alpha_i)^{0.5}(a_j \alpha_j)^{0.5}(1-k_{ij}) \qquad\qquad (\ 28\ )$$

$$b = \sum_{i=1}^{N} y_i b_i$$

where:

$y_i, y_j$     are the mole fractions of components $i$ and $j$ for the phase under consideration (liquid or vapour)
$k_{ij}$     is the binary interaction coefficient[13] between components $i$ and $j$
$N$     is the number of components in the mixture

The pure component parameters are given by

$$b_i = \frac{b_{const}RT_c}{P_c} \quad , \quad a_i = \frac{a_{const}R^2 T_c^2}{P_c}$$

---

[13] Binary interaction coefficients are normally expressed as $k_{ij}$ in the literature. The use of $c_{ij} = 1 - k_{ij}$ is peculiar to the old DNV implementation in PRP where the input values need to be for $c_{ij}$. The reason for this is the somewhat obscure use of the interaction parameters for more than one purpose. They can also be used in the non-ideal mixing rules for simple temperature dependent properties.

where

| Equation of state | $u$ | $a_{const}$ | $b_{const}$ | $\alpha_i$ | $f_w$ |
|---|---|---|---|---|---|
| Redlich Kwong | 0 | 0.4278 | 0.0867 | $\sqrt{T_c/T}$ | |
| Soave Redlich Kwong | 0 | 0.42747 | 0.08664 | $\left[1 + f_w(1 - \sqrt{T/T_c})\right]^2$ | $f_w = 0.48508 + 1.55171\omega - 0.15613\omega^2$ (Graboski & Daubert, 1978) |
| Peng Robinson | 1 | 0.45724 | 0.0778 | $\left[1 + f_w(1 - \sqrt{T/T_c})\right]^2$ | $f_w = 0.37464 + 1.542261\omega - 0.26992\omega^2$ |

**Table 6: Value of Constants for the Cubic Equations of State**

where:

$T_c$      is the critical temperature for the material (K)
$P_c$      is the critical pressure for the material (N/m$^2$)
$T_r$      is the reduced temperature ($T/T_c$)
$\omega$      is the acentric factor for the material, a constant given by:

$$\omega = -\log_{10}\left[\frac{P_{sat}(T = 0.7T_c)}{P_c}\right] - 1 \qquad (29)$$

where $P_{sat}(T)$ is the saturation pressure at the specified temperature (i.e. at 0.7 $T_c$).

The above application of equations of state to mixtures involves the use of mixing rules to calculate the parameters of the equation from the pure component values and composition. Other than this, the fundamental expressions for the calculation of the derived properties are the same for mixtures as for pure materials.

This approach is limited in its applicability to homogenous mixtures that do not react or separate, and that do not exhibit polar effects; some non-ideality can be taken into account, but the range and precision are limited.

Both the Soave Redlich-Kwong and the Peng-Robinson equation give good results for mixtures of non-polar or slightly polar components. The binary interaction constants $k_{ij}$ must be determined from equilibrium data. For hydrocarbon mixtures the $k_{ij}$ may be taken to be zero. The binary interactions are not very important for bulk phase calculations but may be quite significant in equilibrium $K$-value calculations. Even mixtures that are fairly non-ideal may be successfully treated if specific binary interaction constants are derived from measured equilibrium data. Graboski and Daubert (1978) give suggested values for interaction parameters of several non-hydrocarbon gases.

Treatment of supercritical components for Soave-Redlich-Kwong equation
Improved results can be obtained for supercritical components by modifying the functional form for the calculation of $\alpha$. Graboski and Daubert (1979) suggest the following extrapolation for hydrogen:

$$\alpha_{H_2} = c_1 \exp\left[c_2 \frac{T}{T_{c,H_2}}\right] \qquad (30)$$

with $c_1 = 1.202$, $c_2 = -0.30228$
The model currently uses the Mathias (1983) correlation for some other common supercritical components (N$_2$, CO$_2$, H$_2$S, CO):

$$\alpha = \exp\left[c\left(1 - \left[\frac{T}{T_c}\right]^d\right)\right] \quad \text{for } T_r = \frac{T}{T_c} > 1 \qquad (31)$$

$$c = \frac{f_\omega}{d} \qquad (32)$$

$$d = 1 + \frac{f_\omega}{2}$$

(33)

<u>Cubic equation of state for compressibility Z</u>

The cubic equation ( 27 ) can be re-stated as an equation in Z=(PV)/(RT),

$$1 = \frac{1}{Z - B^*} - \frac{A^*}{Z(Z + B^*) + uB^*(Z - B^*)}$$

(34)

Where

$$A^* = \frac{a\alpha P}{R^2 T^2} \text{ and } B^* = \frac{bP}{RT}$$

(35)

This can be rearranged to give the cubic in Z of:

$$Z^3 + C_2 Z^2 + C_1 Z + C_0 = 0$$

(36)

With

$$C_2 = uB^* - 1$$
$$C_1 = A^* - B^*(u+1) - B^{*2}(2u+1)$$
$$C_0 = uB^{*2}(B^* + 1) - A^* B^*$$

(37)

The above cubic equation of state can have 1 or 3 real roots, depending on the values of the coefficients. In the latter case, the minimum root is the liquid compressibility, and the maximum root the vapour compressibility. In the former case, the two property systems diverge in their approaches[14]. The solution in these cases is discussed in detail in Appendix E.

<u>Summary</u>
The Soave-Redlich-Kwong and Peng-Robinson equations are quite similar, and there is little to recommend the use of one over the other. However, the slightly more complicated form of the attraction term in the Peng-Robinson equation is thought to allow a more accurate representation of liquid phase properties.

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[14] CORRECTED. The old property system approach has no physical meaning, and appears to have been chosen largely to avoid discontinuities in properties. A more conventional approach is taken in the new property system. VI4291.

## 3.4 Derivation of mixture properties

Thermodynamic properties for the vapour mixture or the liquid mixture can be derived from the equation of state for the mixture. The basic premise of the equation of state approach is that the same model (same equation of state) should be used to calculate the thermodynamic properties (densities, fugacities, enthalpy departures and entropy departures) for all phases. In the specific case of vapour-liquid equilibrium, the requirement is that the selected equation of state should be able to model adequately both vapour and liquid phase.

The derivation of each property for the mixture is described below.

### 3.4.1 Compressibility and density

The compressibility of the mixture (Z) is calculated from the equation of state, as discussed in the previous section. The density ρ (kmol/m$^3$) is determined from Z using the equation

$$\rho = \frac{1}{V} = \frac{P}{ZRT} \tag{38}$$

For liquids, equations of state may not be very accurate at predicting density, so the Costald method is also available, calculating liquid density as the inverse of the molar volume calculated by the Thomson equation:

$$V = V_s \left( 1 - C \ln \left( \frac{B + P}{B + P_{sat}} \right) \right) \tag{39}$$

Where

$V_{sat}$ = molar volume calculated from the saturated liquid density in section 2.1.2

$P_{sat}$ = saturated vapour pressure calculated as function of temperature T as in section 2.1.2

And the C and B parameters are given by:

$$C = 0.0861488 + 0.0344483\omega \tag{40}$$

$$B = P_c \left( -1 + \sum_{k=1}^{4} A_k (1 - T_r)^{k/3} \right) \tag{41}$$

Where $\omega$ is the acentric factor as defined by equation (29) and the A parameters are:

$$A_1 = -9.070217 \tag{42}$$

$$A_2 = 62.45326 \tag{43}$$

$$A_3 = -135.1102 \tag{44}$$

$$\ln(A_4) = 4.79594 + 0.250047\omega + 1.14188\omega^2 \tag{45}$$

### 3.4.2 Enthalpy and entropy

General
Vapour or liquid enthalpy and entropy[15,16] are calculated using the standard departure functions as derived from the Maxwell equations:

By definition [see e.g. Section 5.3 in Reid et. al. (1987)]

---

[15] CORRECTED. The wrong gas constant (in terms of units) was used in the old property system for the calculation of ideal gas entropy, thus absolute entropies cannot be compared between new and old systems, though Δs terms used in the models will be very similar. VI3710.

[16] DOC. The method described in this section is applied for old property system for the vapour enthalpy/entropy evaluation only. Different methods are applied for evaluation of the liquid enthalpy and entropy

$$A - A_{ref} = -\int_{V_{ref}}^{V} P dV = -\int_{\infty}^{V} \left[ P - \frac{RT}{V} \right] dV - RT \ln\left( \frac{V}{V_{ref}} \right)$$ ( 46 )

$$S - S_{ref} = -\left( \frac{\partial (A - A_{ref})}{\partial T} \right)_v$$ ( 47 )

$$H - H_{ref} = RT(Z-1) + (A - A_{ref}) + T(S - S_{ref})$$ ( 48 )

where

A = Helmholtz function (J/kmol)
S = Entropy (J/kmol/K)
H = Enthalpy (J/kmol)

The subscript "ref" refers to the reference state, which corresponds to an ideal gas with the same pressure P, the same temperature T, and the same composition. Thus, according to the ideal gas law, the reference volume $V_{ref}$ is given by,

$$V_{ref} = \frac{RT}{P} = \frac{V}{Z}$$ ( 49 )

The vapour enthalpy $H_v$ and liquid enthalpy $H_L$ at a given temperature and pressure are calculated by making a correction to the enthalpy of the ideal gas $H_{ig}=H_{ref}$:

$$H_v(T,P) = H_{ref}(T,P) + \Delta H_v(T,P)$$ ( 50 )

$$H_L(T,P) = H_{ref}(T,P) + \Delta H_L(T,P)$$ ( 51 )

$$H_{ref}(T,P) = H_{ig}(T) = \sum_1^N y_i \int_{T_{REF}}^{T} C_{p,ig}^i(T) dT$$ ( 52 )

where:

$C_{p,ig}^i(T)$    is the ideal gas heat capacity of the component (J/kmol.K) as a function of temperature, obtained from its DIPPR® equation.
$T_{REF}$    is a reference temperature, set as 298.16 K
$\Delta H(T,P)$    is the correction to the ideal gas enthalpy, or the "enthalpy departure function".

Similarly, the vapour entropy $S_v$ and liquid entropy $S_L$ at a given temperature and pressure are calculated by making a correction to the entropy of the ideal gas $S_{ig}=S_{ref}$

$$S_v(T,P) = S_{ref}(T,P) + \Delta S_v(T,P)$$ ( 53 )

$$S_L(T,P) = S_{ref}(T,P) + \Delta S_L(T,P)$$ ( 54 )

$$S_{ref}(T,P) = S_{ig}(T,P) = \sum_1^N y_i \int_{T_{REF}}^{T} \frac{C_{p,ig}^i(T)}{T} dT - R\sum_1^N y_i \ln(y_i) - R\ln(\frac{P}{P_{REF}})$$ ( 55 )

where additionally

$P_{REF}$    is a reference pressure, set as 1 Pa

The program first iterates to find the value of the compressibility $Z$ that satisfies the equation of state at the specified pressure and temperature. Given $Z$ it can then obtain $\Delta H$ and $\Delta S$. The liquid departure functions may be obtained from an equation of state that represents the liquid phase adequately.

The enthalpy departure function $\Delta H=H-H_{ref}$ and the entropy departure function $\Delta S=S-S_{ref}$ for a particular phase is calculated from the equation of state, as indicated below for the different equations of state.

#### Ideal equation

Since this assumes no dependence on pressure, the enthalpy departure for the ideal method is zero, and the enthalpy is calculated as the ideal gas enthalpy using the appropriate DIPPR equation. As with enthalpy the entropy departure for an ideal mixture is zero.

#### Virial equation

Applying the virial equation of state ( 23 ) into Equations **( 46 )**, **( 47 )**, **( 48 )** leads to:

$$A - A_{ref} = -\int_{\infty}^{V} \left[ \frac{BRT}{V^2} \right] dV - RT \ln\left(\frac{V}{V_{ref}}\right) = \frac{BRT}{V} - RT \ln Z \tag{56}$$

$$S - S_{ref} = R\left[ \ln Z - \frac{1}{V}\left(B + TB\frac{dB}{dT}\right) \right] = R\left[ \ln Z - \frac{P}{ZRT}\left(B + TB\frac{dB}{dT}\right) \right] \tag{57}$$

$$H - H_{ref} = \frac{RT}{V}\left(B - T\frac{dB}{dT}\right) = \frac{P}{Z}\left(B - T\frac{dB}{dT}\right) \tag{58}$$

#### Cubic equation

Applying the cubic equation of state ( 27 ) into Equations **( 46 )**, **( 47 )**, **( 48 )** leads to:

$$A - A_{ref} = -\int_{\infty}^{V}\left[ \frac{RT}{V-b} - \frac{RT}{V}\frac{a\alpha}{V(V+b)+ub(V-b)} \right]dV - RT\ln\left(\frac{V}{V_{ref}}\right) \tag{59}$$

$$= -RT\ln\frac{V-b}{V} + \frac{a\alpha}{bx_r}\ln\left(\frac{V+bx_p}{V+bx_q}\right) - RT\ln(\frac{V}{V_{ref}})$$

$$S - S_{ref} = R\ln\frac{V-b}{V} - \frac{1}{bx_r}\ln\left(\frac{V+bx_p}{V+bx_q}\right)\frac{d(a\alpha)}{dT} + R\ln(\frac{V}{V_{ref}}) \tag{60}$$

$$= R\ln(z - B^*) - \frac{1}{bx_r}\ln\left(\frac{Z+B^*x_p}{Z+B^*x_q}\right)\frac{d(a\alpha)}{dT}$$

$$H - H_{ref} = \frac{1}{bx_r}\ln\left(\frac{V+bx_p}{V+bx_q}\right)(a\alpha - T\frac{d(a\alpha)}{dT}) + RT(Z-1) \tag{61}$$

$$= \frac{1}{bx_r}\ln\left(\frac{Z+B^*x_p}{Z+B^*x_q}\right)(a\alpha - T\frac{d(a\alpha)}{dT}) + RT(Z-1)$$

Where B* is defined by Equation ( 35 ) and

$$x_r = \sqrt{(u+1)^2 + 4u} \quad , \quad x_p = \frac{u+1-x_r}{2} \quad , \quad x_q = \frac{u+1+x_r}{2} \tag{62}$$

### 3.4.3 Fugacity coefficient[17]

<u>General</u>
According to Section 5.8 in Reid et el. (1987), the fugacity coefficient $\phi_i$ for component $i$ in the mixture is given by

$$\hat{\varphi}_{i,V} = \frac{f_{i,V}}{y_i P} \quad , \quad \hat{\varphi}_{i,L} = \frac{f_{i,L}}{x_i P} \tag{63}$$

$$RT \ln(\hat{\varphi}_i) = \left( \frac{\partial(nA - nA_{ref})}{\partial n_i} \right)_{T,\overline{V},n_{j[i]}} - RT \ln\left( \frac{P}{P_{ref}} \right) \tag{64}$$

Here $f_i$ is the fugacity, and n are mole amounts such that $n = \sum n_i$ ; and $\overline{V} = nV$ . The partial derivative indicates that the temperature T, the total system volume V, and all mole numbers (except i) are to be held constant.
The condition for phase equilibrium is $f_{i,V} = f_{i,L}$, and therefore

$$\frac{y_i}{x_i} = \frac{\hat{\varphi}_{i,V}}{\hat{\varphi}_{i,L}} \tag{65}$$

<u>Ideal method</u>
For the ideal method, the vapour fugacity coefficient $\phi_{i,V} = 1.0$ Moreover,

$$\frac{y_i}{x_i} = \frac{P_{sat}(T)}{P} \tag{66}$$

Therefore the liquid fugacity is given by

$$\hat{\varphi}_{i,L} = \frac{P}{P_{sat}(T)} \tag{67}$$

<u>Virial Equation</u>
The Virial equation is not used for phase equilibrium in this system and so does not need a fugacity coefficient.

<u>Cubic equation</u>
The fugacity coefficient is used in the cubic equation only.

In terms of moles ( i.e. replacing V with $\overline{V} = nV$ ) , the cubic equation ( 27 ) and the Helmholtz energy equation **( 59 )** can be rewritten as

$$P = \frac{nRT}{\overline{V} - nb} - \frac{n^2 a\alpha}{\overline{V}(\overline{V} + nb) + unb(\overline{V} - nb)} \tag{68}$$

$$nA - nA_{ref} = RT\left\{ -n\ln(\overline{V} - nb) + X + n\ln(\overline{V}_{ref}) \right\} \tag{69}$$

Where

$$X = \frac{1}{RT} \frac{n^2 a\alpha}{nbx_r} \ln\left( \frac{\overline{V} + nbx_p}{\overline{V} + nbx_q} \right) \tag{70}$$

Using

---

[17]DOC. The old property system does not use a fugacity coefficient.

$$\frac{\partial(nb)}{\partial n_i} = b_i \qquad (71)$$

and Equation ( 69 ) into Equation ( 64 ) it now follows that

$$
\begin{aligned}
\ln(\hat{\varphi}_i) &= \frac{1}{RT}\left(\frac{\partial(nA - nA_{ref})}{\partial n_i}\right)_{T,\overline{V},n_{j[i]}} - \ln\left(\frac{P}{P_{ref}}\right) \\
&= -\ln(\overline{V} - nb) + \frac{nb_i}{\overline{V} - nb} + \frac{\partial X}{\partial n_i} + \ln(\overline{V}_{ref}) - \ln\frac{P}{P_{ref}} \\
&= -\ln(\frac{P\overline{V} - nbP}{P_{ref}\overline{V}_{ref}}) + \frac{nb_i}{\overline{V} - nb} + \frac{\partial X}{\partial n_i} \\
&= -\ln(Z - B^*) + \frac{b_i}{V - b} + \frac{\partial X}{\partial n_i}
\end{aligned} \qquad (72)
$$

Defining $\lambda$ (while making use of Equation ( 28 )) by

$$\lambda = \frac{1}{n}\frac{\partial(n^2 a\alpha)}{\partial n_i} = 2(a_i\alpha_i)^{0.5}\sum_j\left\{y_j(a_j\alpha_j)^{0.5}(1 - k_{ij})\right\} \qquad (73)$$

and using (see Equation ( 62 ))

$$x_p - x_q = -x_r \ , \quad x_p + x_q = u + 1 \ , \quad x_p x_q = -u \qquad (74)$$

it follows upon differentiation of Equation ( 70 ) that

$$
\begin{aligned}
RT\frac{\partial X}{\partial n_i} &= \frac{n^2 a\alpha}{nbx_r}\left[\frac{x_p b_i}{(\overline{V} + nbx_p)} - \frac{x_q b_i}{(\overline{V} + nbx_q)}\right] + \\
&\quad \frac{1}{(nbx_r)^2}\left[nbx_r\frac{\partial(n^2 a\alpha)}{\partial n_i} - n^2 a\alpha\frac{\partial(nbx_r)}{\partial n_i}\right]\ln\left(\frac{\overline{V} + nbx_p}{\overline{V} + nbx_q}\right) \\
&= -\frac{n^2 a\alpha b_i}{nb}\left[\frac{\overline{V}}{\overline{V}(\overline{V} + nb) + unb(\overline{V} - nb)}\right] \\
&\quad + \frac{1}{nbx_r}\left[n\lambda - na\alpha\frac{b_i}{b}\right]\ln\left(\frac{V + bx_p}{V + bx_q}\right) \\
&= \frac{b_i}{b}\left[PV - \frac{VRT}{V - b}\right] + \frac{1}{nbx_r}\left[n\lambda - na\alpha\frac{b_i}{b}\right]\ln\left(\frac{V + bx_p}{V + bx_q}\right) \\
&= RT\frac{b_i}{b}\left[Z - \frac{V}{V - b}\right] + \frac{a\alpha}{bx_r}\left[\frac{\lambda}{a\alpha} - \frac{b_i}{b}\right]\ln\left(\frac{V + bx_p}{V + bx_q}\right)
\end{aligned} \qquad (75)
$$

Using Equation ( 75 ) into ( 72 ) it now follows that

$$\ln \phi_i = -\ln(Z - B^*) + \frac{b_i}{(V-b)} + \frac{b_i}{b}\left[Z - \frac{V}{V-b}\right] +$$

$$\frac{a\alpha}{bx_r RT}\left[\frac{\lambda}{a\alpha} - \frac{b_i}{b}\right]\ln\left(\frac{V + bx_p}{V + bx_q}\right)$$

$$= -\ln(Z - B^*) + \frac{b_i}{b}(Z - 1) + \frac{A^*}{B^* x_r}\left(\frac{\lambda}{a\alpha} - \frac{b_i}{b}\right)\ln\left(\frac{z + B^* x_p}{z + B^* x_q}\right)$$

( 76 )

The program first iterates to find the value of the compressibility $Z$ that satisfies the equation of state at the specified pressure and temperature, as described in Appendix A. Given $Z$ it can then obtain $\phi_I$ using the above equation.

### 3.4.4 Isothermal Compressibility[18]

General
Using V = RTZ/P, it follows that the isothermal compressibility is defined by

$$\left(\frac{\partial V}{\partial P}\right)_T = RT\frac{\partial}{\partial P}\left(\frac{Z}{P}\right)_T = \frac{RT}{P^2}\left[P\left(\frac{\partial Z}{\partial P}\right)_T - Z\right]$$

( 77 )

Ideal method
Using Z=1, it follows that

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} = -\frac{V}{P}$$

( 78 )

Virial equation
By means of differentiation of Equation ( 24 ), one can solve for $(\partial Z/\partial P)_T$. Using this in Equation ( 77 ), leads to

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{RT}{P^2}\left[\frac{BP}{RT(2Z-1)} - Z\right] = \frac{1}{P}\left[\frac{B}{2Z-1} - V\right]$$

( 79 )

Cubic equation
By means of differentiation of Equation ( 36 ) one can solve for $(\partial Z/\partial P)_T$. Using this in Equation ( 77 ), leads to

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{RT}{P^2}\left[-P\left(\frac{\left(\frac{\partial C_2}{\partial P}\right)_T Z^2 + \left(\frac{\partial C_1}{\partial P}\right)_T Z + \left(\frac{\partial C_0}{\partial P}\right)_T}{3Z^2 + 2C_2 Z + C_1}\right)_T - Z\right]$$

( 80 )

Where

$$\left(\frac{\partial C_2}{\partial P}\right)_T = u\left(\frac{\partial B^*}{\partial P}\right)_T = \frac{uB^*}{P}$$

(81)

---

[18] This is currently not yet implemented.

$$\left(\frac{\partial C_1}{\partial P}\right)_T = \left(\frac{\partial A^*}{\partial P}\right)_T - \left[(u+1) + 2B^*(2u+1)\right]\left(\frac{\partial B^*}{\partial P}\right)_T$$

$$= \frac{A^* - B^*(u+1) - 2B^{*2}(2u+1)}{P}$$

$$\left(\frac{\partial C_0}{\partial P}\right)_T = \left(3uB^{*2} + 2uB^* - A\right)\left(\frac{\partial B^*}{\partial P}\right)_T - B^*\left(\frac{\partial A^*}{dP}\right)_T$$

$$= \frac{uB^*(3B^* + 2) - 2A^*B^*}{P}$$

### 3.4.5 Coefficient of Thermal Expansion[19]

<u>General</u>
Using V = RTZ/P, it follows that the coefficient of thermal expansion is defined by

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}\frac{\partial}{\partial P}(TZ)_T = \frac{R}{P}\left[T\left(\frac{\partial Z}{\partial T}\right)_P + Z\right]$$

( 82 )

<u>Ideal method</u>
Using Z=1, it follows that

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} = \frac{V}{T}$$

( 83 )

<u>Virial equation</u>
By means of differentiation of Equation ( 24 ), one can solve for $(\partial Z/\partial T)_P$. Using this in Equation ( 82 ) leads to

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T}\left[\frac{T\left(\frac{\partial B}{\partial T}\right)_P - B}{(2Z-1)} + V\right]$$

( 84 )

<u>Cubic equation</u>
By means of differentiation of Equation ( 36 ) one can solve for $(\partial Z/\partial T)_P$. Using this in Equation ( 82 ) leads to

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}\left[-T\left(\frac{\left(\frac{\partial C_2}{\partial T}\right)_P Z^2 + \left(\frac{\partial C_1}{\partial T}\right)_P Z + \left(\frac{\partial C_0}{\partial T}\right)_P}{3Z^2 + 2C_2 Z + C_1}\right)_T + Z\right]$$

( 85 )

Where

$$\left(\frac{\partial C_2}{\partial T}\right)_{P:} = u\left(\frac{\partial B^*}{\partial T}\right)_P = -\frac{uB^*}{T}$$

( 86 )

$$\left(\frac{\partial C_1}{\partial T}\right)_P = \left(\frac{\partial A^*}{\partial T}\right)_P - \left[(u+1) + 2B^*(2u+1)\right]\left(\frac{\partial B^*}{\partial T}\right)_P$$

$$= \frac{-2A^* + B^*(u+1) + 2B^{*2}(2u+1)}{T} + \frac{A^*}{\alpha}\left(\frac{d\alpha}{dT}\right)$$

$$\left(\frac{\partial C_0}{\partial T}\right)_P = \left[3uB^{*2} + 2uB^* - A^*\right]\left(\frac{\partial B^*}{\partial T}\right)_P - B^*\left(\frac{\partial A^*}{\partial T}\right)_P$$

$$= \frac{-uB^{*2}(3B^* + 2) + 3A^*B^*}{T} - \frac{A^*B^*}{\alpha}\left(\frac{d\alpha}{dT}\right)$$

---

[19] This is currently not yet implemented.

### 3.4.6 Specific Heat Capacities[20]

General

$$C_v(T,P) = c_{p,ig}(T) - R + R\left[\frac{\Delta C_v(T,P)}{R}\right] \tag{87}$$

$$C_p(T,P) = c_{p,ig}(T) + R\left[\frac{\Delta C_p(T,P)}{R}\right] \tag{88}$$

$$\left[\frac{\Delta C_p(T,P)}{R}\right] = \left[\frac{\Delta C_v(T,P)}{R}\right] - \frac{T}{R}\frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} - 1 \tag{89}$$

Ideal solution
To add
Virial solution
To add
Cubic solution
To add

## 3.4.7 Ratio of Specific Heats

The ratio of specific heats (Cp/Cv = $\gamma$) is calculated from the ideal gas heat capacity (section 1.1.2) using the equation[21]

$$\frac{C_p}{C_v} = \frac{C_{p,ig}}{C_{p,ig} - R} = \gamma \tag{90}$$

## 3.4.8 Vapour or Liquid sonic velocity

The velocity of sound [m/s] through a fluid is the square root of the derivative of pressure with respect to density at constant entropy:

$$c = \sqrt{\left(\frac{dP}{d\rho}\right)_S} \tag{91}$$

For ideal gases, the speed of sound is simply given by:

$$c = \sqrt{\frac{\gamma P}{\rho}} \tag{92}$$

For single-phase real fluids, the speed of sound can be expressed analytically as (Picard and Bishnoi, 1987):

$$c = \sqrt{\frac{\gamma}{k\rho}} \tag{93}$$

Where $\gamma$ is the ratio of specific heats, i.e., based on real fluid properties and $k$ [ms$^2$/kg] is the isothermal coefficient of volumetric expansion: $k$ can be expressed as (Walas, 1987):

$$k = -\rho\left(\frac{\partial V}{\partial P}\right)_T \tag{94}$$

---

[20] DOC. This section needs to be further completed. Currently there is no logic for non-ideal specific heat in XPRP.

[21] This equation for the ratio of specific heats is only applicable to an ideal gas

Note that $\gamma$ and $k$ can be obtained analytically from relevant equations of state (see sections 3.4.4 and 3.4.6).

Alternatively, the derivative in equation ( 91 ) is calculated numerically by perturbing the pressure and finding the temperature that produces a negligible change in entropy, i.e.

- Calculate $s_v(T,P)$ and $\rho_v(T,P)$
- Iteratively calculate $s_v(T+\Delta T, P+\Delta P)$ where the value of dT is estimated in each iteration from (ds/dT) until $s(T,P) = s(T+\Delta T, P+\Delta P)$
- Calculate $\rho_v (T+dT, P+dP)$
- Calculate c from the equation above

This method uses a perturbation in pressure of 1% of the input value, and a convergence tolerance on entropy of 1 J/kmol.K. Note that the numerical approach may be applied in determining the sonic velocity in two-phase, homogenously mixed fluids as well (Mahgerefteh et al., 1999).

## 3.4.9  Saturated and liquid properties (old PRP)

In the old property system (PRP) equation of state methods were not employed for the calculation of liquid properties at all. Instead, they were done by alternative methods, usually involving a departure from the vapour state via the heat of vapourisation.

Although these old methods have been implemented as a non-recommended option in the new property system, the theory behind them is not always valid. Many of the equations used have validity only for a pure component.

For example, many of the methods make use of the saturated vapour pressure. For mixtures this is calculated by a simple mixing rule on the component vapour pressures and therefore corresponds to the bubble point pressure that would be obtained from ideal fugacities. The use of this ideal bubble point pressure when calculating vapour properties can give rise to serious problems for wide boiling mixtures or those containing non-condensable gases.

HEAT OF VAPORISATION

The latent heat of vaporisation is calculated from the Clapeyron-Clausius equation,

$$\frac{dP_{sat}}{dT} = \frac{H_v - H_L}{T(V_v - V_L)}$$

( 95 )

Rearranging this equation yields the following expression for the heat of vaporisation:

$$\Delta H_{vap} = T(V_v - V_L)\frac{dP_{sat}}{dT}$$

( 96 )

The molar volume of the liquid $V_L$ is obtained from the DIPPR® equation for the saturated liquid density, and the derivative of the saturation pressure is obtained by differentiation of its DIPPR® equation[22]. The vapour volume is calculated from the chosen equation of state.

For mixtures, the liquid volume and derivative of the vapour pressure are calculated by simple mixing rules from the pure component data. Strictly speaking, there is no such thing as "heat of vapourisation" for a mixture because it does not change phase at constant temperature and pressure.

Saturated Vapour Enthalpy
This is calculated as described for the vapour enthalpy, with pressure set to the saturated vapour pressure $P_{sat}$ for the specified temperature T.

For mixtures, the vapour pressure is calculated by a simple mixing rule from the pure component data. This means that the calculation is performed at the ideal bubble point of the mixture. This can cause serious problems for wide-boiling mixtures or those containing inert gases such as N2.

---

[22] CORRECTED.  In SAFETI 6.4 and earlier versions this was wrongly calculated for mixtures. VI6413.

## Saturated Liquid Enthalpy
This is calculated as follows:

$$H_L(T, P_{sat}) = H_V(T, P_{sat}) - \Delta H_{vap} \tag{97}$$

where:

$H_v(T, P_{sat})$   is the saturated vapour enthalpy at the specified temperature, calculated as described above.
$\Delta H_{vap}$   is the latent heat of vaporisation, calculated as described above.

## Liquid Enthalpy
The enthalpy for liquid at a given temperature and pressure is derived from the saturated liquid enthalpy given above:

$$H_L(T, P) = H_L(T, P_{sat}) - \Delta H \tag{98}$$

$$
\begin{aligned}
dH &= TdS + VdP \\
&= T\left(\left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT\right) + VdP
\end{aligned} \tag{99}
$$

Using Maxwell's equations and considering the change in enthalpy at a constant temperature, this can be expressed as:

$$dH = \left(-T\left(\frac{\partial V}{\partial T}\right)_P + V\right)dP \tag{100}$$

We are assuming that the liquid is incompressible, so the volume at any pressure is equal to the saturation volume, and:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{dV_{sat}}{dT} \tag{101}$$

Therefore:

$$\Delta H = \Delta P\left(V - T\frac{dV_{sat}}{dT}\right) \tag{102}$$

$$H_L(T, P) = H_L(T, P_{sat}) + (P - P_{sat})\left(V - T\frac{dV}{dT}\right) \tag{103}$$

*V and dV/dT* are obtained from the DIPPR Equation for the liquid density[23], and also the saturated vapour pressure $P_{sat}$, is derived from its DIPPR equation.

## Saturated Vapour Entropy
This is calculated as described for the vapour entropy, with pressure set to the saturated vapour pressure $P_{sat}$ for the specified temperature T.

## Saturated Liquid Entropy
Change in entropy is defined by:

---

[23] CORRECTED.  VI6406.  Derivative of liquid volume was inconsistently done in the old system for supercritical extrapolations: V was constant, but dV/dT ≠ 0.

$$\Delta S = \frac{\Delta Q}{T}$$ ( 104 )

where $\Delta Q$ is the change in heat content.
The saturated liquid entropy is calculated from the saturated vapour enthalpy as follows:

$$S_L(T, P_{sat}) = S_V(T, P_{sat}) - \frac{\Delta H_{vap}}{T}$$ ( 105 )

where:

$s_V(T, P_{sat})$ is the saturated vapour entropy at the specified temperature, calculated as described above.
$\Delta H_{vap}$ is the heat of vaporisation, calculated as described above.

Liquid Entropy
The entropy of the liquid at given temperature and pressure can be derived from the saturation entropy by integrating with respect to pressure at constant temperature. From Maxwell's equations:

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$ ( 106 )

Assuming that liquids are incompressible, this is constant:

$$S_L(T, P) = S_L(T, P_{sat}) - (P - P_{sat})\frac{dV}{dT}$$ ( 107 )

$dV/dT$ is obtained from the DIPPR Equation for the liquid density.
The saturated liquid entropy $S_L(T, P_{sat})$ is calculated as described above.

Saturated Vapour Density
This is calculated as described for the vapour density, with pressure set to the saturated vapour pressure $P_{sat}$, for the specified temperature T.

## 3.5 Special treatment for special chemicals

### 3.5.1 Property evaluation for HF including effects of acid association

This theory has been developed in a general manner to model the effects of association on the physical properties of the associating material. The model will only consider the formation of dimers, trimers, hexamers and octamers. Additionally the model is only applicable to pure components. Association is not
modelled for mixtures.

The model was developed for hydrogen fluoride, and should not be used for any other material.

The Oligomerisation Model
The vapour pressure for the material is defined as being the sum of the partial pressures of its subspecies:

$$P_v = P_1 + P_2 + P_3 + P_6 + P_8$$ ( 108 )

The vapour pressure is obtained from DIPPR® equation 101 using the standard DIPPR® coefficients.
The equilibrium relationship is defined by:

$$K_2 = \frac{P_2}{P_1^2}$$

<div align="right">( 109 )</div>

$$K_3 = \frac{P_3}{P_1^3}$$

$$K_6 = \frac{P_6}{P_1^6}$$

$$K_8 = \frac{P_8}{P_1^8}$$

The equilibrium constants are found using regression from experimental data to fit the equation:

$$K_p = \exp\left\{ A_p - \frac{B_p}{T} \right\}$$

<div align="right">( 110 )</div>

Thus:

$$P_v = P_1 + K_2 P_1^2 + K_3 P_1^3 + K_6 P_1^6 + K_8 P_1^8$$

<div align="right">( 111 )</div>

The mole fractions in the vapour phase of each of the subspecies are given by:

$$y_1 = P_1 \ / \ P_v$$

<div align="right">( 112 )</div>

$$y_2 = P_2 \ / \ P_v$$

$$y_3 = P_3 \ / \ P_v$$

$$y_6 = P_6 \ / \ P_v$$

$$y_8 = P_8 \ / \ P_v$$

such that:

$$y_1 + y_2 + y_3 + y_6 + y_8 = 1$$

<div align="right">( 113 )</div>

Substituting ( 112 ) into ( 111 ) gives:

$$P_v = y_1 P_v + K_2 ( y_1 P_v )^2 + K_3 ( y_1 P_v )^3 + K_6 ( y_1 P_v )^6 + K_8 ( y_1 P_v )^8$$

<div align="right">( 114 )</div>

Equation ( 114 ) can be rearranged to give the following polynomial for $y_1$:[24]

$$y_1 + K_2 P_v y_1^2 + K_3 P_v^2 y_1^3 + K_6 P_v^5 y_1^6 + K_8 P_v^7 y_1^8 = 1$$

<div align="right">( 115 )</div>

and the program performs an iteration to obtain the value of $y_1$.that satisfies this equation, and given $y_1$ it can then calculate the mole fractions of the other subspecies from the relations given above.

Association Factor, f
The association factor, *f*, is defined as:

---

[24] JUSTIFY. VI4292. According to this theory the vapour pressure for the material $P_v$ is calculated for the partial pressures of the subspecies and is thus dependent on temperature alone. In both old and new property systems, however, $P_v$ is not calculated but is an input directly to the method

$$f = y_1 + 2y_2 + 3y_3 + 6y_6 + 8y_8 \qquad (116)$$

Average Molecular Weight, $M_{ave}$
The average molecular weight of the vapour is calculated as follows:

$$M_{ave} = f\,M_1 \qquad (117)$$

where $M_1$ is the molecular weight of the monomer, obtained from the properties database[25].

Vapour Volume
The vapour volume is derived from the vapour volume of the monomer and the association factor by:

$$V_v = \frac{V_1}{f} \qquad (118)$$

Heat of Vaporisation
The latent heat of vaporisation is calculated from the Clapeyron-Clausius equation using a differentiated form of the DIPPR® equation for the saturated vapour pressure. The Clapeyron-Clausius equation is:

$$\frac{dP_{sat}}{dT} = \frac{H_v - H_L}{T(V_v - V_L)} \qquad (119)$$

Rearranging this equation yields the following expression for the heat of vaporisation:

$$\Delta H_v = T(V_v - V_L)\frac{dP_{sat}}{dT} \qquad (120)$$

The molar volume of the liquid $V_L$ is obtained from its DIPPR® equation using standard, and the derivative of the saturation pressure is obtained by differentiation of its DIPPR® equation.

Enthalpy
The enthalpy calculations are based on the saturated liquid enthalpy which is derived from the liquid heat capacity; the saturated vapour enthalpy is calculated by adding the heat of vaporisation to the saturated liquid enthalpy, and the vapour enthalpy is then found by approximating the heat of association and adding this to the saturated vapour enthalpy.

- Saturated Liquid Enthalpy
  The saturated liquid enthalpy is found from the integral of the liquid heat capacity from a reference temperature, $T_{ref}$, to the current temperature, $T$:

$$H_L(T_{sat}) = \int_{T_{ref}}^{T} C_{p,L}\,dT \qquad (121)$$

The integral of the liquid heat capacity is evaluated by integration of its DIPPR® equation.

- Saturated Vapour Enthalpy
  The saturated vapour enthalpy is calculated from the liquid enthalpy by adding the heat of vaporisation:

$$H_v(T_{sat}) = H_L(T_{sat}) + \Delta H_v \qquad (122)$$

- Vapour Enthalpy at Pressure

---

[25] VI4290. The correction factor is not currently used. The DIPPR value is used directly.

The vapour enthalpy at pressure is given by:

$$H_v(T, P) = H_v(T_{sat}, P) + \int_{T_{sat}}^{T} C_{p,v} dT + \Delta H_{asc}$$

<div align="right">( 123 )</div>

However, there is no expression available for the heat capacity of the oligomer vapour from which the integral can be evaluated, so an alternative approach is required.

At a given pressure the vapour tends to become monomeric as the temperature increases. The vapour enthalpy at a given pressure of monomeric vapour is equal to the saturated liquid enthalpy plus the heat of vaporisation of the material assuming it is all monomer plus the heat of association and the integral of the monomer heat capacity from the saturation temperature to the temperature in question.

The approach taken starts with the saturated vapour enthalpy. The enthalpy of the vapour at a temperature where the vapour is wholly composed of monomer is then the saturated vapour enthalpy plus the integral of the monomer heat capacity plus the difference between the heat of vaporisation from liquid to the oligomer vapour and the heat of vaporisation from liquid to monomeric vapour. This last term is derived in a similar fashion as the heat of vaporisation (Equation ( 120 )) and is here termed the heat of association:

$$\Delta H_{asc} = T(V_1 - V_v)\frac{dP_{sat}}{dT}$$

<div align="right">( 124 )</div>

The integral of the monomer heat capacity is obtained by differentiation of DIPPR® equation 107 and using standard DIPPR® coefficients for vapour heat capacity. The vapour enthalpy at a given pressure is then approximated by assuming a temperature range over which the vapour goes from saturation conditions to being purely monomeric vapour, $\Delta T_{asc}$.

The vapour enthalpy is then approximated by:

$$H_v(T, P) = H_{vsat} + x\left[\int_{T_{sat}}^{T} C_{p,1} dT + \Delta H_{asc}\right]$$

<div align="right">( 125 )</div>

where:

$$x = \frac{T - T_{sat}}{\Delta T_{asc}} \quad T_{sat} < T < T_{sat} + \Delta T_{asc}$$

$$x = 1.0 \quad\quad T > T_{sat} + \Delta T_{asc}$$

$$x = 0 \quad\quad\quad otherwise$$

### Entropy
A similar "bottom up" approach is used in calculating entropies.

- Saturated Liquid Entropy
  The saturated liquid entropy is defined as:

$$S_L(T_{sat}) = \int_{T_{ref}}^{T_{sat}} \frac{C_{p,L}}{T} dT$$

<div align="right">( 126 )</div>

where the integral is evaluated using DIPPR® equation 100 for the liquid heat capacity.

- Saturated Vapour Entropy
  The saturated vapour entropy is derived from the saturated liquid entropy the heat of vaporisation:

$$S_v\left(T_{sat}\right) = S_L\left(T_{sat}\right) + \frac{\Delta H_v}{T}$$

( 127 )

- Vapour Entropy at Pressure
  This is derived in a similar fashion to the saturated vapour entropy using the change in enthalpy from saturation conditions given in Equation ( 123 ). So:

$$S_v\left(T,P\right) = S_v\left(T_{sat}\right) + \frac{x}{T}\left[\int_{T_{sat}}^{T} C_{p,L}\,dT + \Delta H_{asc}\right]$$

( 128 )

## 3.5.2 Property evaluation for ammonia including reaction with water[26]

The program uses the model of Raj and Reid (1978) to calculate the enthalpy for a material that reacts with water. This model was developed for the reaction between ammonia and water and should not be used for any other material.

The liquid-water enthalpy $H_{L,W}$, in J/kg, at atmospheric pressure is given by a cubic expansion:

$$H_{L,W} = A_{L,W} + x_L B_{L,W} + x_L^2 C_{L,W} + x_L^3 D_{L,W}$$

( 129 )

where:

$x_L$         is the mass fraction of liquid in the liquid-water aqueous solution

$A, B, C, D$     are constants set for the material in the properties database

The modified partial enthalpy of water, $H'_W$, and the modified partial liquid enthalpy, $H'_L$, are then the partial derivatives of the liquid-water enthalpy at constant pressure with respect to changes in the mass fraction of water and of liquid respectively:

$$H'_W = A_{L,W} - x_L^2 C_{L,W} + 2x_L^3 D_{L,W}$$

( 130 )

$$H'_L = \left(A_{L,W} + B_{L,W}\right) + 2x_L C_{L,W} + x_L^2\left(2D_{L,W} - C_{L,W}\right) - 2x_L^3 D_{L,W}$$

( 131 )

## 3.5.3 Property evaluations for solid phase $CO_2$

The phase diagrams of water and $CO_2$ are included below. It has a critical temperature of 304.2K above which it is always vapour and a triple point of 5.1 atmosphere and 216.6K below which all non-vapour CO2 will be solid.

---

[26] DOC. These are not properties in the normal sense, and are not included in the new property system. They used only by the pool vaporisation calculations.

**Carbon dioxide**
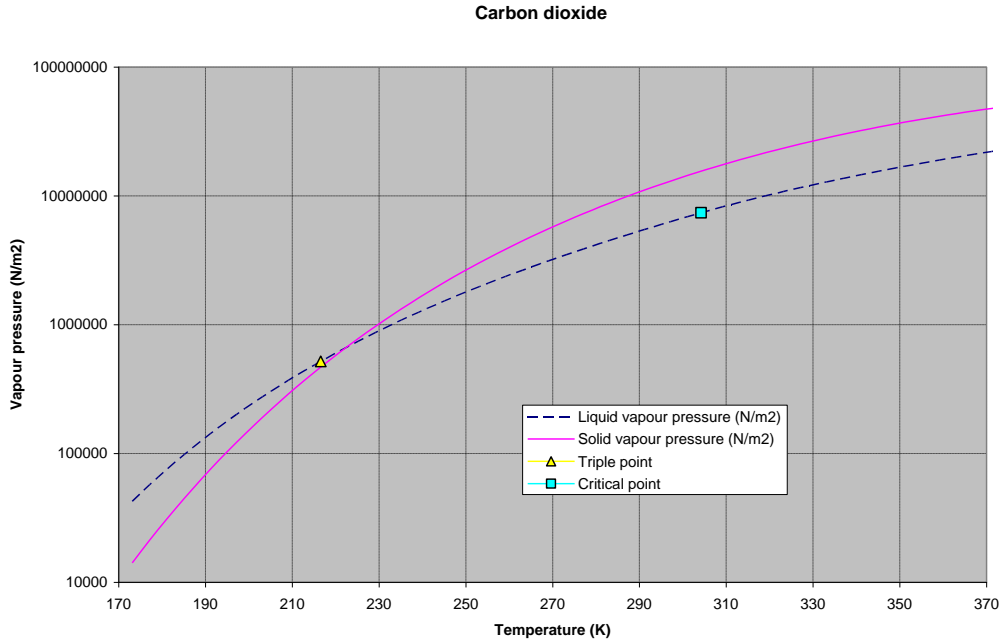
**Figure 2. Liquid and solid vapour pressure curves for CO₂**

The atmospheric expansion (ATEX) and outdoor dispersion (UDM) models allow for the formation of solid phase $CO_2$. To do this they require solid phase properties not supported for other materials.

A number of new 'combination' properties have been introduced for $CO_2$, and these are described below. The approach is to define a 'non-vapour' property, which either uses liquid or solid property, depending on the temperature.

Saturated vapour pressure and saturated vapour temperature
The saturated vapour pressure of the component, $P_{n,sat}(T)$ is set as:

- the vapour pressure $P_{s,sat}(T)$ for solid-vapour equilibrium for $T < T_{melt}$
- the vapour pressure $P_{L,sat}(T)$ for liquid-vapour equilibrium, $T > T_{melt}$ (liquid)

In the DIPPR property database including in PHAST, $T_{melt}$ equals the melting temperature at 1 bar for chemicals with triple-point pressure lower or equal to 1 bar; this is the case for water. Otherwise it equals the triple-point temperature; this is the case for carbon dioxide.

The "liquid" and vapour pressure curve $P_{L,sat}(T)$ and "solid" vapour pressure curve $P_{s,sat}(T)$ obtained from the property system for $CO_2$ and water are given by Figure 2.

$P_{n,sat}$ at a given temperature is thus the minimum of the solid and liquid vapour pressures at that temperature shown in the figures. The "combination" saturated vapour temperature, $T_{n,sat}(P)$, is the inverse of $P_{n,sat}(T)$, i.e. the maximum temperature of the two curves for a given pressure P.

Non-vapour enthalpy
The specific enthalpy (J/kg) of the non-vapour $h_n(T)$ is set as follows:

$$h_n(T) = h_L(T) \qquad\qquad for\ T > T_{melt}\ (liquid) \qquad\qquad \textbf{( 132 )}$$

$$= h_L(T_{melt}) - \Delta h_{fus} - \int_{T}^{T_{melt}} C_{Ps}{}^{DIPPR}(\tau)\,d\tau \qquad for\ T < T_{melt}\ (solid)$$

Here the discontinuity $\Delta h_{fus}$ in enthalpy at the melting point $T_{melt}$ is the enthalpy of fusion $\Delta h_{fus}$ (J/kg). The DIPPR solid heat capacity $C_{Ps}{}^{DIPPR}(T)$ decays virtually linearly between the temperatures $T_{melt}$ and $T_o = 183.15K$.

Therefore it can be approximated by

$$C_{Ps}(T) \approx C_{Ps}{}^{DIPPR}(T_{melt}) - \alpha_s[T_{melt} - T]\ , \quad for\ T < T_{melt} \qquad\qquad \textbf{( 133 )}$$

with

$$\alpha_s = \frac{C_{Ps}{}^{DIPPR}(T_{melt}) - C_{Ps}{}^{DIPPR}(T_0)}{T_{melt} - T_0} \tag{134}$$

Thus the integral in the above equation is evaluated as

$$\int_T^{T_{melt}} C_{Ps}{}^{DIPPR}(\tau)\, d\tau \approx C_{Ps}{}^{DIPPR}(T_{melt})\,[T_{melt} - T] - \frac{1}{2}\,\alpha_s(T_{melt} - T)^2 \tag{135}$$

Therefore it can be approximated by

$$C_{Ps}(T) \approx C_{Ps}{}^{DIPPR}(T_{melt}) - \alpha_s[T_{melt} - T], \quad for\ T < T_{melt} \tag{136}$$

with

$$\alpha_s = \frac{C_{Ps}{}^{DIPPR}(T_{melt}) - C_{Ps}{}^{DIPPR}(T_0)}{T_{melt} - T_0} \tag{137}$$

Thus the integral in the above equation is evaluated as

$$\int_T^{T_{melt}} C_{Ps}{}^{DIPPR}(\tau)\, d\tau \approx C_{Ps}{}^{DIPPR}(T_{melt})\,[T_{melt} - T] - \frac{1}{2}\,\alpha_s(T_{melt} - T)^2 \tag{138}$$

Non-vapour entropy
The entropy of a solid ($S_s$) is given by

$$S_s = \int_0^T \frac{C_p}{T}\, dT \tag{139}$$

Non-vapour entropy can be calculated in a manner analogous to enthalpy:

$$s_n(T) = s_L(T) \qquad\qquad\qquad for\ T > T_{melt}\ (liquid) \tag{140}$$

$$= s_L(T_{melt}) - \frac{\Delta h_{fus}}{T_{melt}} - \int_T^{T_{melt}} \frac{C_{Ps}{}^{DIPPR}(\tau)}{\tau}\, d\tau \qquad for\ T < T_{melt}\ (solid)$$

If we use the same approximation as for enthalpy (i.e. that solid heat capacity $C_{Ps}{}^{DIPPR}$ decays virtually linearly with temperature), then

$$\int_T^{T_{melt}} \frac{C_{Ps}{}^{DIPPR}(\tau)}{\tau}\, d\tau \approx \int_T^{T_{melt}} \frac{C_{Ps}{}^{DIPPR}(T_{melt}) - \alpha_s[T_{melt} - \tau]}{\tau}\, d\tau \tag{141}$$

This evaluates to

$$\int_{T}^{T_{melt}} \frac{C_{Ps}{}^{DIPPR}(\tau)}{\tau} d\tau \approx \alpha_s \left( T - T_{melt} \right)$$

( 142 )

Where

$$\alpha_s = \frac{C_{Ps}{}^{DIPPR}(T_{melt}) - C_{Ps}{}^{DIPPR}(T_0)}{T_{melt} - T_0}$$

( 143 )

Non-vapour density
In a manner analogous to non-vapour enthalpy, non-vapour density $\rho_n$ is a new property. Solid density uses a DIPPR temperature equation.

$$
\begin{aligned}
\rho_n(T,P) &= \rho_L(T,P) & for\ T > T_{melt}\ (liquid) \\
&= \rho_s(T) & for\ T < T_{melt}\ (solid)
\end{aligned}
$$

( 144 )

# 4. CALCULATION OF PHASE EQUILIBRIUM FOR A MIXTURE

This section describes the theory used in FLAS, the new module which performs rigorous phase-equilibrium calculations for multi-component streams.

## 4.1    Phase equilibrium for a multi-component stream

The general case of phase equilibrium in the flashing of a multi-component stream is shown in Figure 3. A multi-component mixture stream of given molar flow *F*, overall composition (mole fractions) **z**, temperature $T_0$ and pressure $P_0$ is flashed at a temperature T and a pressure *P* with exchange of heat *Q* (which may be zero). This process produces a vapour stream (of molar flow V and composition **y**) and a liquid stream (of molar flow L and composition x).
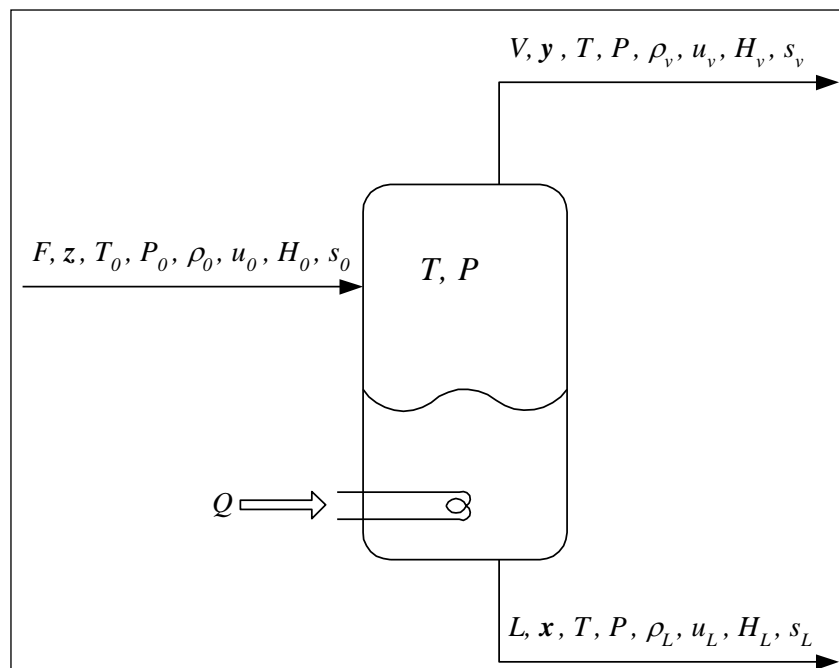


**Figure 3: Equilibrium between Vapour and Gas in Multi-Component Flash**

Some of the flash conditions are known (e.g. *T* and *P*), and the model calculates the remaining conditions (e.g. V, *L*, **y** and **x**). Five types of flash calculation are performed, with different known and unknown quantities for each type:

1.  *Isothermal flash* or flash at specified temperature *T* and pressure *P*.

    This is a very useful calculation for a variety of situations. It can be used in phase identification / scenario definition before a consequence calculation. Calculation of mixed-phase stream thermodynamic properties (enthalpies, entropies) is dependent on an isothermal flash.

2.  *Isentropic flash* or flash at specified entropy *s* and pressure *P*.

    This is a reversible adiabatic flash and it can be used in situations usually approximated by a reversible process e.g. an orifice expansion between the bulk of the fluid and the vena contracta.

3.  *Isenthalpic flash* or flash at specified enthalpy *H* and pressure *P*.

    This is an irreversible adiabatic flash and it can be used in processes with high degree of irreversibility e.g. the discharge through a pipe (which involves considerable friction) can be modelled with an energy balance, which, in turn, can be converted to an equivalent enthalpy balance. This is only an example where the isenthalpic flash can be a useful function for the solution of problem but it is not implied that discharge problems can generally be reduced to phase equilibrium problems.

4.  *Constant Energy flash* or flash at specified energy *E* ($H + 0.5u^2$) and pressure *P*.

    The energy *E* is given by ($H + 0.5u^2$) where *u* is the flow velocity. This is a generalisation of the isenthalpic flash. The constant energy flash is used in discharge modelling for adiabatic but irreversible expansions, when the kinetic energy

cannot be neglected. e.g. expansion from the stagnation point to the pipe orifice and for the expansion from the pipe orifice to the atmosphere.

5. *Constant vapour fraction flash* or flash at specified P & Vapour fraction (Ψ) or T & Ψ.

   This includes dew / bubble pressures and temperatures. This can also be very useful in phase identification /scenario identification and in a variety of consequence models.

The details of these calculations are described below.

## 4.2 Mathematical formulation

The flash process assumes equilibrium between the vapour phase and the liquid phase, which means that the 2 phases have the same temperature (*T*) and pressure (*P*) and the total Gibbs free energy *G* of the 2-phase system is minimised:

$$\underset{\mathbf{y},\mathbf{x},V,L}{MIN}[G(T,P,\mathbf{y},\mathbf{x},V,L)]$$

**( 145 )**

subject to mass balance and other equality and inequality constraints. The optimisation variables are different depending on the specified parameters.

As it is shown in standard textbooks (e.g. Section 4 in Perry and Green, 1997, Perry's Chemical Engineers' Handbook, 1973) assuming that the 2-phase system is closed and there is no chemical reaction, minimisation of the total Gibbs free energy is equivalent to equalities between the vapour-phase component chemical potentials and the respective liquid-phase component chemical potentials:

$$\mu_{v,i}(T,P,\mathbf{y}) = \mu_{L,i}(T,P,\mathbf{x}) \qquad \text{for all } i=1,NC$$

**( 146 )**

where *NC* is the number of components in the mixture

It can easily be shown that this is equivalent to an equality between each vapour phase component fugacity ($f_{v,i}$) and the respective liquid phase component fugacity ($f_{L,i}$):

$$f_{v,i}(T,P,\mathbf{y}) = f_{L,i}(T,P,\mathbf{x}) \qquad \text{for all } i=1,NC$$

**( 147 )**

If an equation of state approach is used for the calculation of the fugacities of both phases then the fugacities are calculated from the equations:

$$f_{v.i} = \hat{\phi}_{v,i}(T,P,\mathbf{y}) y_i P \qquad \text{for all } i=1,NC$$

**( 148 )**

$$f_{L.i} = \hat{\phi}_{L,i}(T,P,\mathbf{x}) x_i P \qquad \text{for all } i=1,NC$$

**( 149 )**

where $\hat{\phi}_{v,i}$ and $\hat{\phi}_{L,i}$ are the vapour and liquid fugacity coefficients for component *i*, calculated from the equation of state as shown in Equations ( 262 ) to ( 265 ).

Equation ( 147 ) is usually written in terms of vapour and liquid phase mole fractions and the equilibrium K-value:

$$K_i(T,P,\mathbf{y},\mathbf{x}) = \frac{y_i}{x_i} \qquad \text{for all } i=1,NC$$

**( 150 )**

Then K-values can be calculated from the equation:

$$K_i(T,P,\mathbf{y},\mathbf{x}) = \frac{\hat{\phi}_{L,i}(T,P,\mathbf{x})}{\hat{\phi}_{v,i}(T,P,\mathbf{y})}$$

( 151 )

The flash process of **Figure** 3 is also described by the following equations:

*Overall material balance:*

$$F = V + L$$

( 152 )

*Component material balance:*

$$z_i F = y_i V + x_i L$$

( 153 )

*Vapour Phase Mole Fractions:*

$$\sum_i^{NC} y_i = 1$$

( 154 )

*Liquid Phase Mole Fractions:*

$$\sum_i^{NC} x_i = 1$$

( 155 )

*Molar Vapour Fraction:*

$$\Psi = \frac{V}{F}$$

( 156 )

*Enthalpy Balance:*

$$H(T,P,\mathbf{y},\mathbf{x}) - H_0(T_0,P_0,\mathbf{y}_0,\mathbf{x}_0) - \Delta H = 0$$

( 157 )

$$H(T,P,\mathbf{y},\mathbf{x}) = \Psi\, H_v(T,P,\mathbf{y}) + (1-\Psi)\, H_L(T,P,\mathbf{x})$$

( 158 )

The vapour and liquid enthalpies $H_v$ and $H_L$ for the mixture are calculated from the equation of state, as described in Equations ( 50 ) to ( 254 )

*Entropy Balance:*

$$S(T,P,\mathbf{y},\mathbf{x}) - S_0(T_0,P_0,\mathbf{y}_0,\mathbf{x}_0) - \Delta S = 0$$

( 159 )

$$S(T,P,\mathbf{y},\mathbf{x}) = \Psi\, S_v(T,P,\mathbf{y}) + (1-\Psi)\, S_L(T,P,\mathbf{x})$$

( 160 )

The vapour and liquid entropies $S_v$ and $S_L$ for the mixture are calculated from the equation of state, as described in Equations ( 53 ) to ( 257 ).

*Energy Balance:*

$$E(T, P, \mathbf{y}, \mathbf{x}) - E_0(T_0, P_0, \mathbf{y}_0, \mathbf{x}_0) - \Delta E = 0 \tag{161}$$

$$E(T, P, \mathbf{y}, \mathbf{x}) = \Psi \, E_v(T, P, \mathbf{y}) + (1 - \Psi) \, E_L(T, P, \mathbf{x}) \tag{162}$$

$$E_0(T, P, \mathbf{y}, \mathbf{x}) = H_0(T, P, \mathbf{y}) + \frac{1}{2} u_0^2 \tag{163}$$

$$E_L(T, P, \mathbf{y}, \mathbf{x}) = H_L(T, P, \mathbf{y}) + \frac{1}{2} u_L^2 \tag{164}$$

$$E_v(T, P, \mathbf{y}, \mathbf{x}) = H_v(T, P, \mathbf{y}) + \frac{1}{2} u_v^2 \tag{165}$$

The vapour and liquid enthalpies $H_v$ and $H_L$ for the mixture are calculated from the equation of state, as described Equations ( 50 ) to ( 254 ).

## 4.3 Solving the phase-equilibrium Equations: literature review

The method used to solve the phase-equilibrium equations shown in Section 4.3 depends to some extent on the type of calculation that is being performed (i.e. which quantities are known and which are required), and on the equations involved. Broadly there are 2 approaches of solution:

- *Approach A: Numerical solution of a system of non-linear equations.*

  This normally involves the equilibrium equations (Equations ( 147 ) or ( 150 )), the material balance equations or similar (Equations ( 152 ) to ( 155 )) and possibly an additional equation such as the vapour fraction specification (Equation ( 156 )), the enthalpy balance (Equations ( 157 ) and ( 158 )) or the entropy balance (Equations ( 160 ) and( 159 )).
  This is the most widely used approach and it has also been used in this work.

- *Approach B: Constrained minimisation of the Gibbs free energy G.*

  The minimisation includes a number of equality constraints such as the material balance equations or similar (Equations ( 152 ) to ( 155 )) and possibly an additional equation such as the vapour fraction specification (Equation ( 156 )), the enthalpy balance (Equations ( 157 ) and ( 158 )) or the entropy balance (Equations ( 160 ) and( 159 )). The algorithm also includes some inequality constraints since most of the variables (temperatures, pressures etc.) have to be positive numbers and some other variables (vapour fraction, mole fractions) have their own validity ranges.

  This approach is widely used for the solution of the chemical reaction equilibrium problems and it has been occasionally used for phase equilibrium.

Significant research on the algorithms of solution of the phase equilibrium problem was conducted in the 1970s and 1980s. This was often part of development of flowsheeting programs / process simulators and led to substantial progress in the development and refinement of the algorithms. This progress has been summarised in review papers such as Michelsen (1982b), Heidman (1983) and Ammar and Renon (1987). More recent work has focused on more specialised topics such as phase equilibria of reactive systems (Seider and Widagdo, 1996), calculation of flammability limits using chemical equilibrium (Melhem, 1997) and other limited scope improvements (Vetere, 1996, Michelsen, 1998). Currently there is more effort in the area of improvement of the actual thermodynamic models for a wider range of mixtures.

### 4.3.1 Solution of non-linear equations

Considering the methods of solution of the system of non-linear equations (equation solving approach or approach A), there are two further sub-classes:

*Global Equation-Solving Approach*

The system of all equations (including equilibrium equations and material balances) is solved simultaneously in terms of all the problem unknowns. Characteristic of this approach is that the material balances are not satisfied during iteration.

A well-known formulation following this approach is the one by Asselineau et al (1979) who use a global Newton-Raphson method to solve the system of equations.

The advantage of a global Newton Raphson is that, assuming a good variable initialisation, the algorithm converges rapidly towards a solution, even for points near the critical point. The theoretical convergence rate of Newton Raphson near the solution is quadratic. The disadvantage of the approach is that, in the absence of good initialisation, the algorithm may diverge or converge slowly.

There have been a number of attempts to improve over the global Newton Raphson approach. Some of them use the quasi-Newton approach, where the Jacobean matrix (normally calculated at each iteration in a full global Newton Raphson) is approximated by a matrix, which is updated at each iteration from the previous iteration matrix. There are also hybrid methods such as the one by Joulia et al (1986) which use a slow but safe method in the first step (quasi-linearisation or successive substitution) until the algorithm is relatively near the solution and then, they use a global Newton Raphson or equivalent (quasi-Newton) to speed up convergence. The weakness of these hybrid methods is that they require an empirical criterion to switch from one method to the other and it is not easy to find a good universal criterion.

*Equation-Solving Approach with a Reduced Set of Variables*

A common characteristic of these methods is that the material balance equations are satisfied at each iteration.

The best known of these methods is the Successive Substitution Method (SSM). A version of this method has been used in this work and is discussed in detail in Sections 4.4.1 and 4.4.2.

The convergence characteristics of the SSM have been discussed by several authors, for example by Prausnitz et al (1980) and Michelsen (1982b). The theoretical rate of convergence of the SSM is linear and convergence can become very slow near the critical point if fugacity coefficients are calculated by the same equation of state for all phases. There have been many attempts to accelerate the rate convergence of the SSM. Boston and Britt (1978) used Broyden's method to update the equilibrium K-values between iterations. Michelsen (1982b) used ideas from Crowe and Nishio's (1975) dominant eigenvalue method to accelerate convergence. Acceleration is obviously a desired feature but it should be noted that this often involves the risk of overshooting the solution and entering the infeasible region (e.g. entering the single phase region while iterating on vapour liquid equilibrium problem)

### 4.3.2 Minimisation of Gibbs free energy

The Gibbs minimisation approach (approach B) is theoretically a rigorous approach as it is intended to ensure that the solution is a local minimum of the Gibbs free energy and not simply a stationary point.

Simply solving the system of the equilibrium equations (Equation( 146 )) theoretically ensures that the solution is a stationary point of the Gibbs energy but not necessarily a minimum. However it is worth noting, as Michelsen (1982b) demonstrated, that convergence of the successive substitution method always leads to a local minimum.

A relatively small number of authors have used a Gibbs minimisation technique to solve phase equilibrium problems. Sometimes this was a "by-product" of the use of the minimisation technique on chemical equilibrium problems. Notably Gautam and Seider (1979) and Ohanomah and Thomson (1984) used the RAND quadratic programming optimisation algorithm to solve the problem. Gautam and Seider reported good results while Ohanomah and Thomson (1984) concluded that the method was not so reliable. Melhem (1997) used the Wilson-Han-Powell successive quadratic programming (optimisation) algorithm to solve chemical and phase equilibrium problems.

In our view, there is not enough evidence on the performance, convergence characteristics, the reliability and ease of use of general optimisation techniques for phase equilibrium problems in comparison with the more focused "equation solving" techniques. The success of these optimisation techniques possibly depends to a large extent on the availability of robust and efficient optimisation programs.

### 4.3.3 Choice of method

As the emphasis of this work is on the robustness of the algorithm and the simplicity of implementation, a Successive Substitution Method (SSM) has been chosen and is described in detail in Sections 4.4.1 and 4.4.2.

It should be noted that the conditions of most consequence analysis problems are not in the immediate vicinity of the critical point and, a successive substitution algorithm can be computationally very efficient. In the few cases of operation near the critical point, the SSM will inevitably become slower but it will maintain its stability and robustness.

However, this method cannot readily be applied to phase equilibrium calculations involving more than two phases (e.g. Vapour-Liquid-Liquid) because there are a number of trivial solutions when the phase compositions are identical. If the thermodynamic methods are extended in the future to handle such systems (other than where the second liquid phase is treated as pure water) then it will be necessary to move to a Gibbs Free Energy minimisation solution.

## 4.4 Algorithm adopted for solution of phase-equilibrium equations

### 4.4.1 Isothermal or constant vapour-fraction flash

A common successive substitution algorithm has been developed for the following the problems:

*Isothermal flash.* Temperature $T$ and pressure $P$ are specified and Equations ( 150 ) to ( 156 ) are solved to calculate the vapour fraction $\Psi$, the vapour phase compositions **y** and the liquid phase compositions **x;**

*Vapour fraction and temperature flash.* Temperature $T$ and the vapour fraction $\Psi$ are specified and Equations ( 150 ) to ( 156 ) are solved to calculate the pressure $P$, the vapour phase compositions **y** and the liquid phase compositions **x;**

*Vapour fraction and pressure flash.* Pressure $P$ and the vapour fraction $\Psi$ are specified and Equations ( 150 ) to ( 156 ) are solved to calculate the temperature $T$, the vapour phase compositions **y** and the liquid phase compositions **x.**

The details of the common algorithm, shared by the above three problems, is described in Appendix B. The basic algorithm includes the following steps:

1.  Initialise K-values;
    In the case of the isothermal flash, the Rault law is used.

2.  Initialise the unknown variable $X$ ($\Psi$, $P$ or $T$);

3.  Set the objective function $G(X)$ and solve it with respect to the unknown $X$;
    $X$ is sought so that $G(X)=0$.

4.  Update compositions of the vapour (**y**) and liquid (**x**) phase and possibly the $K$-values
    $\mathbf{K} = \mathbf{K}(T, P, \mathbf{y}, \mathbf{x})$ from the equilibrium and mass balance equations (Equations ( 150 ) to ( 153 )).

5. Iterate steps 3 and 4 until convergence is achieved.

The objective function G($X$) (or equation to solve) and the iterating variable depend on the specific problem:

- *T, P* flash

  The vapour fraction $\Psi$ is the iterating variable while the equation to solve is:

$$G(\Psi) = \sum_i y_i - \sum_i x_i = 0$$

( 166 )

Appendix B describes how the unknown variable $\Psi$ is first bracketed before the Newton Raphson is initiated.

- *P, $\Psi$* flash

  The inverse of the temperature $u\,(=1/T)$ is used as iterating variable. The equation to solve is:

$$G(u) = \ln\left(\frac{\sum_i y_i}{\sum_i x_i}\right)$$

( 167 )

The use of the inverse of the temperature results in a more "linear" equation and facilitates convergence.

- *T, $\Psi$* flash

  The pressure $P$ is the iterating variable while the equation to solve is:

$$G(P) = \sum_i y_i - \sum_i x_i = 0$$

( 168 )

See Appendix B for the detailed equations and their derivation, the initialisation procedure, the Newton-Raphson iteration formula and the convergence criteria.

## 4.4.2 Isenthalpic, isentropic or constant-energy flash

These calculations include the equilibrium and mass balance equations (Equations ( 150 ) to ( 156 )), and also the appropriate balance equations for the type of calculations: Equations ( 157 ) and ( 158 ) for the isenthalpic flash, Equations ( 159 ) and ( 160 ) for the isentropic flash, and Equations ( 161 ) to ( 165 ) for the constant energy flash.

The solution for each of these types of flash calculation is done with a similar successive substitution method, and is all cases the pressure $P$ is the second allowed specification.

The first part of the algorithm determines if the specified total quantity (i.e. the enthalpy, entropy, or energy) is in the range of sub-cooled liquid quantities or in the range of superheated vapour quantities.

If it is confirmed that a single phase is present, then a special single-phase secant algorithm is called to determine the unknown temperature.

If the tests indicate that there are two phases present, the program performs an iteration to determine the unknown variables (i.e. the vapour fraction, the temperature and the compositions of the vapour and liquid phase).

On each iteration, the vapour fraction is varied until the required balance is satisfied (i.e. of enthalpy, entropy or energy), and the iteration can be summarised by the following steps:

1. The vapour fraction is varied in steps of 0.05 until a narrower interval is found where the appropriate balance equation changes sign. The solution is then bracketed and a secant method can commence.

2. A vapour fraction $\Psi$, calculated by the secant formula, is then suggested.

3. The constant vapour fraction flash calculation described in Section 4.4.1 is called to determine a new temperature T and compositions of the vapour and liquid phase. This involves another iteration inside the main iteration (an "inner loop" inside the main "outer loop").

4. The equation error and the variation of $\Psi$ between iterations are checked. If convergence has not been achieved the iteration continues from step 2.

The algorithm is described in detail in Appendix C.


# 5. VERIFICATION AND VALIDATION

This section describes the tests performed to verify the modelling of mixture properties and of phase-equilibrium.

## 5.1 Property and phase equilibrium calculations

Verification of the key new property system thermodynamic methods (i.e. those in the preferred template set of methods), together with VLE calculations (unavailable in the old system) is discussed here[27].

The methods implemented in our new property system, such as the Peng Robinson and the Soave equations of state, have been extensively reviewed in the literature, tested, validated against experimental data and compared with other models and they are still considered a standard in the petroleum industry. Similar considerations apply to the phase equilibrium algorithms used for the solution of the system of equations. Therefore there is no need for any extra validation of the models against experimental data.

The new property system results have been verified against the results of the equivalent models within a standard commercial process design program. The process simulator PRO/II version 4.15 of SimSci (Simulation Sciences Inc) has been selected for this purpose. One mixture was selected for a comprehensive comparison of the various flash problems and mixture properties. This is a mixture of light hydrocarbons consisting mainly of butane, propane and pentane and it was taken from an actual consequence analysis problem. The mixture details are shown in Table 7.

| Name | Light Oil |
|---|---|
| | Composition in % moles |
| Ethane | 0.02 |
| Propane | 23.72 |
| n-Butane | 61.03 |
| n-Pentane | 14.75 |
| n-Hexane | 0.48 |
| Initial temperature (K) | 273.15 |
| Initial Pressure (Pa) | 32.05 x 10$^5$ |
| All binary interaction parameters $c_{ij}$ | 1 |

**Table 7: Light Hydrocarbon Test Mixture, composition and properties**

The first test problem is an isothermal flash of the light oil mixture at 273.15 K and 1 atm, using the Peng Robinson (PR) equation of state. The results are shown in Table 8. The input stream is a sub-cooled liquid kept pressurised. When it expands to atmospheric pressure, it flashes about 70% of the material into the vapour phase. Table 8 shows clearly that the differences between the new property system and PRO/II are very small:

- The difference on both vapour and liquid densities is under 0.1%, which is very small. This is an indication that the same equation of state is solved and the same roots are found;

- The vapour fraction difference is under 1%, which is acceptable;

- The difference on K-values, liquid mole fractions and vapour mole fractions is typically under 1% and this is considered acceptable.
  The main exception to this is the n-hexane K-values and mole fractions, where the percent difference is higher. An explanation of this difference is that the absolute value of the n-hexane K-value is relatively small and this affects the rounding errors and the calculation accuracy in general;

- Absolute enthalpies and entropies were not compared as the two program use different ideal gas reference states.

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[27] For a fuller description see the PROP testing documentation. Other mixtures and cases have been verified, but the results are not included here.

Specifically PRO/II used 1 degree Rankine as ideal gas entropy reference, while the DIPPR equation is not valid at so low temperatures. The comparison is therefore done on the enthalpy (or entropy) difference between the output and input streams: it is the difference of enthalpies and entropies that matters in this type of calculations and not the absolute values. The error (or difference) for both entropies and enthalpies is less than 1%, which is considered acceptable.

| Output | New property system | | | | % Difference: New property system - PRO/II | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | Input Stream | Liquid Output Stream | Vapour Output Stream | Output Stream with H &S changes | Liquid Phase | Vapour Phase | T,P,H,S, VF and K-Value |
| Mass Flow Rate, kmole | 100.00 | 28.86 | 71.14 | 100.00 | | | |
| Temperature, K | 273.15 | 273.15 | 273.15 | 273.15 | | | 0.00% |
| Pressure, Pa | 3.21E+06 | 1.01E+05 | 1.01E+05 | 1.01E+05 | | | 0.00% |
| Vapour Fraction | 0 | 0 | 1 | 0.7079 | | | |
| Δ Enthalpy, J | | | | 1.49E9 | | | 0.67% |
| Density, mol/m3 | 11.084 | 10.371 | 0.046 | 3.024 | -0.09% | 0.01% | |
| Δ Entropy, J/K | | | | 5.73E+06 | | | 0.67% |
| Molecular Mass | 56.99 | 61.91 | 54.97 | 56.99 | 0.07% | 0.06% | |
| Output Vap. Fraction | 0 | 0 | 1 | 0.7079 | | | 0.75% |
| Components | Mole Fractions | | | K-values | Mole Fractions | | K-values |
| n-butane | 0.6103 | 0.6023 | 0.6136 | 1.02E+00 | -0.34% | 0.13% | 0.47% |
| Ethane | 0.0002 | 0.0000 | 0.0003 | 1.85E+01 | -0.64% | -0.69% | -0.05% |
| n-hexane | 0.0048 | 0.0144 | 0.0009 | 6.45E-02 | 2.07% | -2.15% | -4.13% |
| n-pentane | 0.1475 | 0.3126 | 0.0794 | 2.56E-01 | 0.68% | 1.09% | 0.40% |
| Propane | 0.2372 | 0.0708 | 0.3058 | 4.31E+00 | -0.46% | -0.53% | -0.06% |

**Table 8: Flash of light oil (T=273.15K,P=1.013Pa; Peng Robinson)**

The second test problem is the same isothermal flash of the light oil mixture at 273.15 K and 1 atm, but using the SRK-API model (Soave Redlich Kwong - API implementation, Graboski and Daubert, 1978). The results are shown in Table 9. As it is expected the results of SRK equation of state are very similar to the results of the PR equations of state. The differences between new property system and SimSci results are even smaller than with the PR equation. The vapour fraction difference is only 0.23%, which is easily acceptable.

A number of other runs were performed to verify the correctness of implementation of the other phase equilibrium problems. The tables below present the most important output variables from these tests.

| Output | New property system | | | | % Difference: Spreadsheet - PRO/II | | |
| | Input Stream | Liquid Output Stream | Vapour Output Stream | Output Stream with H &S changes | Liquid Phase | Vapour Phase | T,P,H,S, VF and K-Value |
|---|---|---|---|---|---|---|---|
| Mass Flow Rate, kmole | 100.00 | 30.64 | 69.36 | 100.00 | | | |
| Temperature, K | 273.15 | 273.15 | 273.15 | 273.15 | | | 0.00% |
| Pressure, Pa | 3.21E+06 | 1.01E+05 | 1.01E+05 | 1.01E+05 | | | 0.00% |
| Vapour Fraction | 0 | 0 | 1 | 0.6937 | | | |
| Enthalpy, J | | | | 1.48E+09 | | | 0.22% |
| Density, mol/m3 | 9.819 | 9.189 | 0.046 | 2.847 | -0.03% | 0.00% | |
| Entropy, J/K | | | | 5.66E6 | | | 0.21% |
| Molecular Mass | 56.99 | 61.83 | 54.86 | 56.99 | 0.02% | 0.02% | |
| Output Vap. Fraction | | | | 0.6937 | | | 0.23% |
| Components | Mole Fractions | | | K-values | Mole Fractions | | K-values |
| n-butane | 0.6103 | 0.6059 | 0.6122 | 1.01E0 | -0.13% | 0.05% | 0.18% |
| ethane | 0.0002 | 0.0000 | 0.0003 | 1.89E1 | -0.08% | -0.21% | -0.14% |
| n-hexane | 0.0048 | 0.0137 | 0.0009 | 6.20E-2 | 0.95% | -3.27% | -4.18% |
| n-pentane | 0.1475 | 0.3090 | 0.0762 | 2.46E-1 | 0.18% | 0.37% | 0.19% |
| propane | 0.2372 | 0.0713 | 0.3105 | 4.36E0 | 0.11% | -0.19% | -0.30% |

**Table 9: Isothermal flash of light oil (T=273.15K,P=1.013Pa; Soave-Redlich-Kwong (API))**

Table 10 shows the results of the isenthalpic flash. The temperature difference (0.01%) is very small while the vapour fraction (0.27%) is also acceptably small.

Table 11 shows the results of the isentropic flash. There appears to be a good agreement between isentropic temperatures (0.04%). The vapour fraction relative difference (-6.4%) is not negligible and some time was spent investigating the entropy calculation as a possible source of the difference.

However no error was found. In absolute terms, the difference between vapour fractions is 0.005, which is still small.

| Output Variable | New property system | PRO/II Value |
|---|---|---|
| Temperature (K) | 260.16 | 260.20 |
| Vapour Fraction | 0.0909 | 0.0906 |

**Table 10: Isenthalpic flash of light oil (P=1.013Pa; Soave-Redlich-Kwong (API))**

| Output Variable | New property system | PRO/II Value |
|---|---|---|
| Temperature (K) | 259.76 | 259.80 |
| Vapour Fraction | 0.0758 | 0.0756 |

**Table 11: Isentropic flash of light oil (P=1.013Pa; Soave-Redlich-Kwong (API))**

Table **12** and Table **13** show the results of the dew/ bubble pressure and dew/ bubble temperature calculations. The differences range between 0.01% for temperatures and 0.1% for pressures. This is considered a satisfactory agreement.

| Output Variable | New property system | PRO/II Value |
|---|---|---|
| Dew Pressure, Pa | $7.502 \times 10^4$ | $7.520 \times 10^4$ |
| Bubble Pressure, Pa | $1.745 \times 10^5$ | $1.742 \times 10^5$ |

**Table 12: Dew and bubble pressure of light oil (T=273.15K; Soave Redlich Kwong (API))**

| Output Variable | New property system | PRO/II Value |
|---|---|---|
| Dew Temperature (K) | 413.027 | 412.995 |

| Bubble Temperature (K) | 405.30 | 405.26 |
|---|---|---|

**Table 13: Dew and bubble temperature of light oil (P=32.05x10⁵Pa, Soave-Redlich-Kwong (API))**

## 5.1.1 Vapour Sonic Velocity at 0 °C and 1.01325 bar

| Component | DNV property system {PHAST-MC template} [numerical solution] (m/s) | DNV property system {PHAST-MC template} [analytical solution] (m/s) | Literature (Lide, 1994) (m/s) |
|---|---|---|---|
| Air (dry) | 331.54 | 331.79 | 331.45 |
| Ammonia | 415.63 | 415.86 | 415 |
| Carbon Monoxide | 336.83 | 337.07 | 338 |
| Carbon Dioxide | 258.08 | 258.21 | 259 |
| Chlorine | 204.39 | 204.50 | 206 |
| Ethylene | 317.48 | 317.62 | 317 |
| Hydrogen | 1260.38 | 1261.27 | 1284 |
| Methane | 430.55 | 430.79 | 430 |
| Nitrogen | 336.84 | 337.09 | 334 |
| Oxygen | 314.68 | 314.91 | 316 |

## 5.1.2 Vapours at 97.1 °C and 1.01325 bar

| Component | DNV property system {PHAST-MC template} [numerical solution] (m/s) | DNV property system {PHAST-MC template} [analytical solution] (m/s) | Literature (Lide, 1994) (m/s) |
|---|---|---|---|
| Acetone | 237.42 | 237.47 | 239 |
| Benzene | 202.42 | 202.44 | 202 |
| Ethanol | 269.61 | 269.66 | 269 |
| Methanol | 336.38 | 336.50 | 335 |

## 5.2 Acid Association

The theory presented above for acid association modelling has been compared with data from a DuPont manual. Though not reproduced here, a summary of these comparisons has been included in previous PHAST release manuals, *e.g.* PHAST 4.2.

# 6. FUTURE DEVELOPMENTS

The following further work is proposed.

1. Binary interaction parameters

   The property system only allows for one set of binary interaction parameters for a mixture, but these parameters can potentially be used for more than one purpose. They can be used in the calculation simple temperature-dependent properties and in the equations of state (Soave Redlich Kwong and Peng Robinson). Clearly this presents a problem, since the same set of parameters is unlikely to be valid in more than one context. It also means that the convention used for the values of the interaction parameters differs from the normal standards in the literature.

   As it happens, in PHAST 6 the user has no mechanism whereby he can change the mixing rules used for the simple temperature-dependent properties, and so the interaction parameters are never used in this context. They are however shared by the equation of state methods. It would be preferable if a separate set of interaction parameters could be supplied for each method.

2. Water as a separate phase

   Appendix F to this theory manual documents the treatment of water as a separate liquid phase. This should be added to the new property system.

3. Solution algorithms for phase equilibrium

   The current algorithm is fine for systems involving 2-phase (i.e Vapour-Liquid) equilibrium. If, in the future, there is a need to handle 3 (or more) phases (e.g. VLLE) there would probably be a need to move to a Gibbs Energy minimisation technique such as that of Michelson. These have the advantage that there is no a priori assumption about the number of phases present, as they tend to operate in a loop on an ever increasing number of phases:

   a.    Perform minimisation

   b.    Test stability

   c.    If Unstable, increase number of phases and go back to 1.

   Fortunately, the stability test normally produces good estimates for the starting point of the next iteration.

   It should be noted that the chosen SSM method implicitly defines a maximum of two phases. If this is used on a system whose interaction parameters would produce more than two phases, the results from the SSM can be wildly inaccurate. Since only SRK and PR are currently implemented, you are unlikely to get into this problem. However, if you were to implement (say) NRTL as a method for polar mixtures then it becomes quite common.

4. Emulating pseudo-component properties and equilibrium in the new property system

   A number of properties in the new property system are either not appropriate for mixtures (*e.g.* saturated properties, heat of vaporisation) or are calculated by suspect methods (*e.g.* liquid enthalpy, liquid entropy, heat of vaporisation). These obsolete properties and suspect methods are included in the new property system, but should not be used apart from where PHAST 6.4 methods need to be reproduced. It is recommended that new development does not use obsolete properties, and that the preferred template set of methods become the default for use within PHAST / SAFETI. Obsolete properties should be removed when no longer used in any models.

   For equilibrium calculations, the models used a saturation curve $P_{sat}(T)$ to determine the material VLE (this functionality was not provided by the old property system). This logic is now included in the PROP model, but the inclusion of a new fugacity method could mean that the standard property system equilibrium calculation could emulate the results of this. This remains to be tested, and there are concerns that it may prove too slow for use in the models. The approach is documented in Appendix I.

5. Acid association properties

   The acid association properties (specifically acid association factor and molecular weight) appear to be implemented wrongly in comparison to the theory documented here, and in comparison to the experimental data taken from the PHAST 4.2 manual. This issue needs further investigation.

## APPENDICES

## Appendix A.  *Application guidelines for physical property system*

This appendix includes guidelines for applying the physical property system. First a brief recapitulation of basic principles is given as discussed in the body of this report. Subsequently an overview of available 'templates' of properties and methods is given. This e.g. define the methods available for mixing rules of thermodynamic properties.

### *A.1*  Basic Principles

Phase Equilibrium
The mole balance equation for vapour / liquid equilibrium is:

$$z_i = \alpha y_i + (1-\alpha)x_i$$

If we define the equilibrium constant ($K$ value) as

$$K_i = \frac{y_i}{x_i}$$

then the mass balance equation can be rearranged to compute the equilibrium compositions:

$$x_i = \frac{z_i}{1+\alpha(K_i-1)}$$

$$y_i = K_i x_i$$

Therefore, the essence of solving the equilibrium is one of determining the $K$ values.

Fugacity
The fundamental equation governing the vapour / liquid equilibrium of a mixture is very simple – it states that the fugacity of each component must be equal in both phases:

$$f_i^v = f_i^l \qquad (i = 1-n)$$

The problem therefore is one of relating the fugacity of the component in each phase to the independent variables of Temperature($T$) and Pressure($P$).

The methods are as follows:

1.  *The Ideal Solution*
    The simplest method for calculating fugacity is the "ideal" solution which uses a combination of Raoult' law and Daltons's law, such that:

$$f_i^v = y_i P$$

$$f_i^l = x_i P_i^{sat}$$

    When written in terms of the equilibrium constant we obtain:

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P}$$

    This is clearly reasonable in that, for a pure component, the $K$ value is unity (and hence equilibrium is established) when the saturated vapour pressure equals the system pressure – in other words, the component boils.

It is also very convenient because the *K* value depends only on temperature and pressure, and not on the composition of the phases.

The ideal solution model is certainly the most appropriate model for pure components because the saturated vapour pressure equation is normally a correlation of experimental determined data.

It also gives reasonable results for mixtures of non-polar components (e.g. hydrocarbons) at low pressures where the temperatures required to achieve equilibrium will not be far removed from the component boiling points. When these conditions are no longer applicable, different methods of calculating fugacity need to be employed.

2. *Deviation from Ideal Solution*

The ideal solution makes the following assumptions:

- the vapour obeys the ideal gas law $(PV = nRT)$.

- the liquid is incompressible.

- there are no energy interactions between the components.

There are therefore two main reasons for deviations from ideal behaviour:

- volumetric effects – arising largely from operating at elevated pressures

- energetic effects – arising largely from the polar nature of one or more of the components

Historically, these deviations have been tackled in different ways. The volumetric effects have been addressed by using Equations of State to represent the PVT behaviour of the mixture. The energetic effects have been addressed through energy-interaction models (usually only for the liquid phase) leading to the Activity Coefficient models.

Therefore, the appropriate choice of model can be illustrated diagrammatically as:
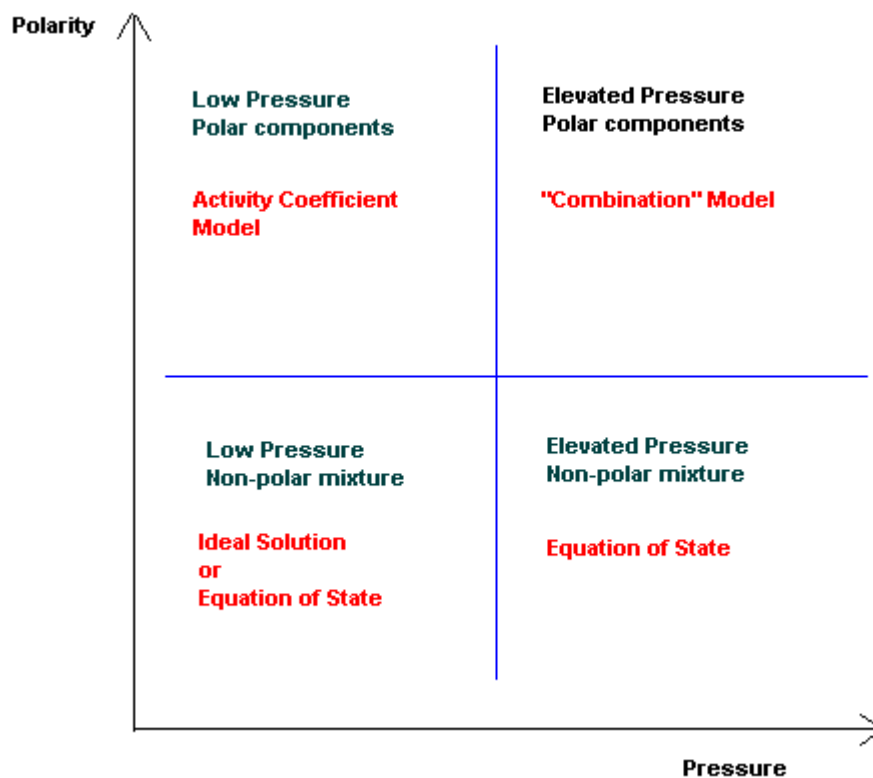


3. *Equations of state*

Many, many equations of state have appeared in the literature – far too many to mention them all. The most frequently used, because they combine relative simplicity with a good degree of accuracy, are the cubic equations of state. Of these, the commonly used ones are:

- Redlich-Kwong (RK)

- Soave-Redlich-Kwong (SRK)

- Peng-Robinson (PR)

These equations are able to represent the PVT behaviour of both the vapour and liquid phases. They are therefore able to completely describe the behaviour of the system at all conditions providing the same EOS is applied to both phases and this would be strongly recommended.

In terms of calculating fugacity, the Soave modification to the RK equation to produce the SRK equation significantly improved its accuracy in predicting vapour / liquid equilibrium and so would normally be used in preference to RK.

The choice between SRK and PR is less clear cut. The performance of both is very similar, and it is usually a question of user preference.

Very often the SRK and PR equations are used without binary interaction parameters with adequate accuracy. Interaction parameters (determined from experimental data, and sometimes available in published literature) can improve the accuracy further for specific circumstances. They can also be used to extend the applicability of the equations to the light gases and slightly polar components that are frequently present in hydrocarbon mixtures e.g. Hydrogen, Nitrogen, Hydrogen Sulphide, Carbon Monoxide, and Carbon Dioxide.

4. *Activity coefficient models[28]*

The three most commonly used Activity coefficient models are:

- Wilson

- NRTL (Non-Random, Two Liquid)

- UNIQUAC (Unified Quasi Chemical)

Of these, the Wilson equation is the only one that is not capable of also representing liquid / liquid equilibrium in partially miscible systems. However, this is largely irrelevant (and sometimes an advantage) when no 3-phase flash algorithm is available.

The models only apply to the liquid phase fugacity. The method for the vapour phase is chosen separately. However, because generally the activity coefficient model is only applicable at low pressure, it is often sufficient to use the ideal model for the vapour phase. Whatever choice is made, the fact that the models are different means that you can never achieve the correct predictions for near-critical behaviour.

To use an activity coefficient model successfully, binary interaction parameters are essential. Without them, the model reverts effectively to the ideal solution model. Therefore, the choice of model is often determined by the availability of suitable interaction parameters.

When binary interaction parameters are unavailable, the UNIFAC method can be used either in total, or more commonly, to fill in the missing pairs by estimating the interaction parameters for one of the models above. UNIFAC is based on the UNIQUAC equation but works in terms of functional groups (e.g. CH3, OH, etc) rather than components. The interaction parameters between functional groups have been determined by regression of large amounts of experimental data for many different components, and hence the method is capable of predicting the behaviour of components for which no data is available.

5. *"Combination" models[29]*

Historically, the calculation of equilibrium for polar mixtures at elevated pressures has been a grey area.

Early attempts at representing such systems usually involved the use of mixed methods – e.g. an equation of state for the vapour, and an activity coefficient method for the liquid.

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[28] Note that there are currently no activity coefficient models available in the property system

[29] Note that there are currently no "combination" models available in the property system

Not only are such mixed methods unable to describe near critical conditions, it was also generally necessary to make the liquid phase interaction parameters temperature dependant. But this has the drawback of needing experimental data at elevated temperatures in order to determine the temperature dependency of the parameters.

Attempts were also made to use more complex mixing rules for the parameters of the equations of state.

It is believed that the most successful approach has been that adopted by equations of state based on the Huron-Vidal approach, especially the MHV2 (Modified Huron-Vidal 2$^{nd}$ Order) equation. The essence of such models is as follows:

Take the Gibbs Free Energy expression from an equation of state such as SRK is

$$g_{EOS}^{E} = f_{EOS}(T, P, z)$$

and the Gibbs Free Energy expression from an activity coefficient such as Wilson is

$$g_{ACT}^{E} = f_{ACT}(T, P, z)$$

and formulate that they must be equal.

This gives an expression that is impossible to solve. However, by making certain restrictions (e.g. at zero pressure in MHV2), a more reasonable expression can be obtained that results (with some further approximations) in an expression that gives the parameters of the equation of state as a mixing rule based on the parameters of the activity coefficient model.

This equation of state, with this mixing rule in place, is applied to both the vapour and liquid phases. It can be shown that in mixtures where both low and high pressure experimental data is available, this model is able to quite accurately predict the high pressure data using only interaction parameters derived from the low pressure data.

## *A.2* Application Guidelines

The available methods for selection in the initial implementation of the property system are limited so this section is as much about what cannot be modelled accurately as what can be.

Available Templates
Generally it is not necessary to define a method for each property individually. Instead it is often satisfactory to select from a predefined 'template' of properties and methods. To date the following templates have been defined. Adding more is a simple procedure.

| | |
|---|---|
| Phast 64 | A set of properties and methods mimicking the behaviour of the property system in PHAST version 6.42[30]. Note that for mixtures, all 'constant' properties must be defined. This is the only template available to users in SAFETI 6.5. |
| Phast MC | A set of properties (same list as above) and methods based largely on using Soave Redlioch Kwong where applicable and simple mixing rules are used for other properties. |
| Peng Robinson | A shorter list of properties (excluding DNV properties) where Peng Robinson is used where applicable and simple mixing rules are used for other properties |
| Soave Redlich Kwong | A shorter list of properties (excluding DNV properties) where Soave Redlich Kwong is used where applicable and simple mixing rules are used for other properties |
| Ideal and SRK | The same as above except that the vapour and liquid fugacity methods are set to 'ideal'. |

Available methods
Apart from simple mole and mass mixing rules the following specific methods are available:

| | Vapour | Liquid |
|---|---|---|
| Fugacity | Ideal<br>Soave Redlich Kwong<br>Peng Robinson<br>Redlich Kwong | Ideal<br>Soave Redlich Kwong<br>Peng Robinson<br>Redlich Kwong |
| Density and Compressibility | Ideal<br>Soave Redlich Kwong<br>Peng Robinson<br>Redlich Kwong<br>Virial | Soave Redlich Kwong<br>Peng Robinson<br>Redlich Kwong<br>Costald[(1)] |
| Enthalpy | Ideal<br>Soave Redlich Kwong<br>Peng Robinson<br>Redlich Kwong<br>Virial | Soave Redlich Kwong<br>Peng Robinson<br>Redlich Kwong |
| Entropy | Ideal<br>Soave Redlich Kwong<br>Peng Robinson<br>Redlich Kwong<br>Virial | Soave Redlich Kwong<br>Peng Robinson<br>Redlich Kwong |
| Viscosity | Kouzel | Kendall Monroe |
| NFPA      Flammable<br>Toxic<br>Reactivity | Maximum Component Value | Maximum Component Value |
| Flammable Toxic Flag | DNV | DNV |

Notes:
(1) This implementation uses a simple mixing rule on the DIPPR Saturated Liquid Density coefficients, which is then pressure corrected.

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[30] Some properties have been changed due to errors being fixed or equation of state methods being adopted (combustion $C_t$, flammable/toxic determination, liquid entropy and liquid enthalpy.

All other stream properties use a simple mixing rule. The mixing rule is appropriately chosen from one of mole ideal, mass ideal, mole Le Chatelier or mass Le Chatelier.

Many properties also have a 'constant' method available which means that the property for a phase must be specifically set and will never change until reset. Constant properties are therefore independent of temperature, pressure and composition.

For a detailed description of the methods themselves see the body of this report.

### Equations of state

Equations of state are generally applicable over a wide range of temperature and pressure and find wide use in gas processing and refining applications and some petrochemical applications. They can be used to predict phase behaviour close to the critical point. The equations of state offered here are not applicable when polar components are present or when the concentrations of gases such as H2, N2, CO2, CO and H2S in the liquid phase are higher than a few percent.

Redlich Kwong and Virial have largely been superseded and are included for reasons of backward compatibility with PHAST 6.2. When an equation of state is to be used the choice between Soave Redlich Kwong or Peng Robinson is largely a matter of user preference. The results are very similar except for liquid densities where Peng Robinson is marginally better. In general however, none of the available equations of state are recommended for liquid densities.

### Phase equilibrium calculations
There can only exist a single vapour phase and a single liquid phase. Solid phases and solid equilibrium is not modelled nor are system consisting of two or more immiscible liquid phases.

### Water handling
Water is not treated in any special way. Water is a DIPPR component like any other. Its properties are calculated using whatever methods are selected for a particular property. There are no supported ASME Steam Tables or other specialised methods. Similarly, for equilibrium calculations, water is not treated in any special way that might enable a second liquid phase to exist, be that phase pure water or otherwise.

### Pure component streams
Phase behaviour within the range of the vapour pressure data should be modelled using vapour pressure i.e., ideal fugacities. At temperatures or pressures above the limit of the vapour pressure equation it will be better to use an equation of state such as Soave Redlich Kwong.

### Polar mixtures
Polar mixtures that form azeotropes, more than one liquid phase or mixtures that contain different types of components cannot be modelled accurately using the methods offered here.
At low pressure, phase behaviour for mixtures such as methanol, ethanol, propanol, etc should be modelled using vapour pressure data, i.e., ideal fugacities. These kinds of mixtures are quite well behaved with little interaction between the component species.

### Hydrocarbon applications with light gases
Use Soave Redlich Kwong or Peng Robinson as long as there are no polar components present. If gases such as N2, CO2, H2S, H2 or CO are present then interaction parameters between these components and the hydrocarbons should also be supplied. Use the Costald liquid density method.

### Petrochemical applications

1. *Light hydrocarbons*

   Use Soave Redlich Kwong or Peng Robinson as long as there are no polar components present. If gases such as N2, CO2, H2S, H2 or CO are present then interaction parameters between these components and the hydrocarbons should also be supplied. Use the Costald liquid density method.

2. *Aromatics*

   At low pressures when the components are similar (e.g., xylene isotopes) you can use Ideal fugacity calculations but with increased CPU time you can also use Soave Redlich Kwong or Peng Robinson. Use the Costald liquid density method.

   If non-aromatics are also present the system cannot be accurately modelled using the equations of state currently available here.

# Appendix B. *DIPPR Equations (including derivatives and integrals)*

This Appendix includes a list of the DIPPR equations used for calculating many temperature-dependent properties.

| Equation Number | Equation |
|---|---|
| 100 | $Y = A + BT + CT^2 + DT^3 + ET^4$ |
| 101 | $Y = \exp\left[ A + \dfrac{B}{T} + C\ln T + DT^E \right]$ |
| 102 | $Y = \dfrac{AT^B}{1 + \dfrac{C}{T} + \dfrac{D}{T^2}}$ |
| 104 | $Y = A + \dfrac{B}{T} + \dfrac{C}{T^3} + \dfrac{D}{T^8} + \dfrac{E}{T^9}$ |
| 105 | $Y = \dfrac{A}{B^{[1+(1-T/C)^D]}}$ |
| 106 | $Y = A(1-T_r)^{(B+CT_r+DT_r^2+ET_r^3)}$ |
| 107 | $Y = A + B\left[\dfrac{C/T}{\sinh(C/T)}\right]^2 + D\left[\dfrac{E/T}{\cosh(E/T)}\right]^2$ |
| 114 | $Y = \dfrac{A^2}{(1-T_r)} + B - 2AC(1-T_r) - AD(1-T_r)^2$ $-\dfrac{1}{3}C^2(1-T_r)^3 - \dfrac{1}{2}CD(1-T_r)^4$ $-\dfrac{1}{5}D^2(1-T_r)^5$ |
| 116 | $Y = A + B(1-T_r)^{0.35} + C(1-T_r)^{\frac{2}{3}}$ $+ D(1-T_r) + E(1-T_r)^{\frac{4}{3}}$ |

**Table 14: DIPPR® Equations for temperature-dependent DIPPR properties**

**In**

Table **14**:

| | |
|---|---|
| $Y$ | is the property |
| $T$ | is the temperature, K |
| $T_r$ | is the reduced temperature ($T/T_{critical}$) |

Each material has its own values of the coefficients *A, B, C, D, E* for a given property, defined as constant properties for the material, and obtained from the DIPPR® database. DIPPR also provides the temperature limits for evaluation of the property, and property value at those limits. These are used by the new property system.

The remainder of this appendix includes derivatives and integrals to the above equations, which may be required as part of property evaluations in applications to consequence models.

DIPPR 100

Equation:
$$Y = A + BT + CT^2 + DT^3 + ET^4$$

First Derivative:
$$\frac{dY}{dT} = B + 2CT + 3DT^2 + 4ET^3$$

Second Derivative:
$$\frac{d^2Y}{dT^2} = 2C + 6DT + 12ET^2$$

Integral YdT:
$$\int Y dT = AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} + \frac{ET^5}{5} + K$$

Integral (Y/T)dT:
$$\int \frac{Y}{T} dT = A\ln(T) + BT + \frac{CT^2}{2} + \frac{DT^3}{3} + \frac{ET^4}{4} + K$$

DIPPR 101

Equation:
$$Y = \exp\left( A + \frac{B}{T} + C\ln(T) + DT^E \right)$$

First Derivative:
$$\frac{d(\ln(Y))}{dT} = -\frac{B}{T^2} + \frac{C}{T} + DET^{E-1}$$

$$\frac{dY}{dT} = Y\frac{d(\ln(Y))}{dT}$$

Second Derivative:
$$\frac{d^2(\ln(Y))}{dT^2} = \frac{2B}{T^3} - \frac{C}{T^2} + DE(E-1)T^{E-2}$$

$$\frac{d^2Y}{dT^2} = Y\left( \frac{d^2(\ln(Y))}{dT^2} + \left(\frac{d(\ln(Y))}{dT}\right)^2 \right)$$

Integral YdT:    Not implemented

Integral (Y/T)Dt:  Not implemented

DIPPR 102

Equation:
$$Y = \frac{AT^B}{1 + \frac{C}{T} + \frac{D}{T^2}}$$

First Derivative: Let $U = AT^B$ and $V = 1 + \frac{C}{T} + \frac{D}{T^2}$

Then $\frac{dU}{dT} = ABT^{B-1}$ and $\frac{dV}{dT} = -\frac{C}{T^2} - \frac{2D}{T^3}$. So,

$$\frac{dY}{dT} = \frac{1}{V^2}\left( V\frac{dU}{dT} - U\frac{dV}{dT} \right)$$

Second Derivative:
$$\frac{d^2 U}{dT^2} = AB(B-1)T^{B-2}$$

$$\frac{d^2 V}{dT^2} = \frac{2C}{T^3} + \frac{6D}{T^4}$$

$$\frac{d^2 Y}{dT^2} = \frac{1}{V^2}\left(V\frac{d^2 U}{dT^2} - U\frac{d^2 V}{dT^2}\right) - \frac{2}{V^3}\frac{dV}{dT}\left(V\frac{dU}{dT} - U\frac{dV}{dT}\right)$$

Integral YdT:           Not implemented

Integral (Y/T)dT:  Not implemented

<u>DIPPR 104</u>

Equation:
$$Y = A + \frac{B}{T} + \frac{C}{T^3} + \frac{D}{T^8} + \frac{E}{T^9}$$

First Derivative:
$$\frac{dY}{dT} = -\frac{B}{T^2} - \frac{3C}{T^4} - \frac{8D}{T^9} - \frac{9E}{T^{10}}$$

Second Derivative:
$$\frac{d^2 Y}{dT^2} = \frac{2B}{T^3} + \frac{12C}{T^5} + \frac{72D}{T^{10}} + \frac{90E}{T^{11}}$$

Integral YdT:
$$\int Y dT = AT + B\ln(T) - \frac{C}{2T^2} - \frac{D}{7T^7} - \frac{E}{8T^8}$$

Integral (Y/T)dT:
$$\int \frac{Y}{T} dT = A\ln(T) - \frac{B}{T} - \frac{C}{3T^3} - \frac{D}{8T^8} - \frac{E}{9T^9}$$

<u>DIPPR 105</u>

Equation:
$$Y = AB^{-\left[1+\left(1-\frac{T}{C}\right)^D\right]}$$

First Derivative:   Reformulate as  $\ln(Y) = \ln\left(\frac{A}{B}\right) - \left(1-\frac{T}{C}\right)^D \ln(B)$

Then
$$\frac{d(\ln(Y))}{dT} = \left(\frac{D}{C}\right)\left(1-\frac{T}{C}\right)^{(D-1)}\ln(B)$$

$$\frac{dY}{dT} = Y\frac{d(\ln(Y))}{dT}$$

Second Derivative:
$$\frac{d^2(\ln(Y))}{dT^2} = -\left(\frac{D}{C}\right)\left(\frac{D-1}{C}\right)\left(1-\frac{T}{C}\right)^{(D-2)}\ln(B)$$

$$\frac{d^2 Y}{dT^2} = Y\left(\frac{d^2(\ln(Y))}{dT^2} + \left(\frac{d(\ln(Y))}{dT}\right)^2\right)$$

Integral YdT:           Not implemented

Integral (Y/T)dT:  Not implemented

Notes: 1. Equation cannot be evaluated for T > C, therefore C must be > 0
2. The B coefficient cannot be negative

<u>DIPPR 106</u>

Equation:
$$Y = A(1 - T_r)^{(B + CT_r + DT_r^2 + ET_r^3)}$$

First Derivative:  Reformulate as  $\ln(Y) = \ln(A) + (B + CT_r + DT_r^2 + ET_r^3)\ln(1 - T_r)$

Then if $U = B + CT_r + DT_r^2 + ET_r^3$ , $\dfrac{dU}{dT} = \dfrac{C + 2DT_r + 3ET_r^2}{T_c}$

and if $V = \ln(1 - T_r)$ , $\dfrac{dV}{dT} = -\dfrac{1}{T_c - T}$

$$\frac{d(\ln(Y))}{dT} = U\frac{dV}{dT} + V\frac{dU}{dT}$$

$$\frac{dY}{dT} = Y\frac{d(\ln(Y))}{dT}$$

Second Derivative:
$$\frac{d^2U}{dT^2} = \frac{2D + 6ET_r}{T_c^2}$$

$$\frac{d^2V}{dT^2} = -\frac{1}{(T_c - T)^2}$$

$$\frac{d^2(\ln(Y))}{dT^2} = U\frac{d^2V}{dT^2} + 2\frac{dV}{dT}\frac{dU}{dT} + V\frac{d^2U}{dT^2}$$

$$\frac{d^2Y}{dT^2} = Y\left(\frac{d^2(\ln(Y))}{dT^2} + \left(\frac{d(\ln(Y))}{dT}\right)^2\right)$$

Integral YdT:  Not implemented

Integral (Y/T)dT:  Not implemented

Notes:  Cannot be evaluated if $T_r > 1.0$

Equation:

$$Y = A + B\left[\frac{(C/T)}{\sinh(C/T)}\right]^2 + D\left[\frac{(E/T)}{\cosh(E/T)}\right]^2$$

First Derivative: Let $p = \dfrac{C}{T}$ and $q = \dfrac{E}{T}$

Then $\dfrac{dp}{dT} = -\dfrac{C}{T^2}$ ; $\dfrac{d^2p}{dT^2} = \dfrac{2C}{T^3}$ ; $\dfrac{dq}{dT} = -\dfrac{E}{T^2}$ ; $\dfrac{d^2q}{dT^2} = \dfrac{2E}{T^3}$

Then let $U = \dfrac{p}{\sinh(p)}$ and $V = \dfrac{q}{\cosh(q)}$

Therefore $\sinh(p) = \dfrac{p}{U}$

$$\frac{d(\sinh(p))}{dp} = \cosh(p) = \frac{U - p\dfrac{dU}{dp}}{U^2}$$

$$\frac{dU}{dp} = \frac{U - U^2\cosh(p)}{p}$$

$$\frac{dU}{dT} = \frac{dU}{dp}\frac{dp}{dT}$$

And $\cosh(q) = \dfrac{q}{V}$

$$\frac{d(\cosh(q))}{dq} = \sinh(q) = \frac{V - q\dfrac{dV}{dq}}{V^2}$$

$$\frac{dV}{dq} = \frac{V - V^2\sinh(q)}{q}$$

$$\frac{dV}{dT} = \frac{dV}{dq}\frac{dq}{dT}$$

So $Y = A + BU^2 + DV^2$

$$\frac{dY}{dT} = 2BU\frac{dU}{dT} + 2DV\frac{dV}{dT}$$

Second Derivative: From above $p\dfrac{dU}{dp} = U - U^2\cosh(p)$

Differentiating $\quad p\dfrac{d^2U}{dp^2}+\dfrac{dU}{dp}=\dfrac{dU}{dp}-U^2\sinh(p)-2U\dfrac{dU}{dp}\cosh(p)$

So $\dfrac{d^2U}{dp^2}=\dfrac{-U^2\sinh(p)-2U\dfrac{dU}{dp}\cosh(p)}{p}$

$\dfrac{d^2U}{dT^2}=\dfrac{dU}{dp}\dfrac{d^2p}{dT^2}+\dfrac{d^2U}{dp^2}\left(\dfrac{dp}{dT}\right)^2$

And similarly $\quad q\dfrac{dV}{dq}=V-V^2\sinh(q)$

Differentiating $\quad q\dfrac{d^2V}{dq^2}+\dfrac{dV}{dq}=\dfrac{dV}{dq}-V^2\cosh(q)-2V\dfrac{dV}{dq}\sinh(q)$

So $\dfrac{d^2V}{dq^2}=\dfrac{-V^2\cosh(q)-2V\dfrac{dV}{dq}\sinh(q)}{q}$

$\dfrac{d^2V}{dT^2}=\dfrac{dV}{dq}\dfrac{d^2q}{dT^2}+\dfrac{d^2V}{dq^2}\left(\dfrac{dq}{dT}\right)^2$

And finally $\quad \dfrac{d^2Y}{dT^2}=2B\left[U\dfrac{d^2U}{dT^2}+\left(\dfrac{dU}{dT}\right)^2\right]+2D\left[V\dfrac{d^2V}{dT^2}+\left(\dfrac{dV}{dT}\right)^2\right]$

Integral YdT:

$$\int Y\,dT=AT+\dfrac{BC}{\tanh(C/T)}-DE\tanh(E/T)+K$$

Integral(Y/T)dT:

$$\int\dfrac{Y}{T}\,dT=A\ln(T)+B\left[\dfrac{(C/T)}{\tanh(C/T)}-\ln\left(\sinh(C/T)\right)\right]-D\left[(E/T)\tanh(E/T)-\ln(\cosh(E/T))\right]+K$$

DIPPR 114

Equation:

$$Y=\dfrac{A^2}{X}+B-2ACX-ADX^2-\dfrac{C^2X^3}{3}-\dfrac{CDX^4}{2}-\dfrac{D^2X^5}{5}$$

where $X=1-T_r$

First Derivative: $\quad \dfrac{dY}{dX}=-\dfrac{A^2}{X^2}-2AC-2ADX-C^2X^2-2CDX^3-D^2X^4$

$$\frac{dX}{dT} = -\frac{1}{T_c}$$

$$\frac{dY}{dT} = \frac{dY}{dX}\frac{dX}{dT}$$

Second Derivative:
$$\frac{d^2Y}{dX^2} = \frac{2A^2}{X^3} - 2AD - 2C^2X - 6CDX^2 - 4D^2X^3$$

$$\frac{d^2Y}{dT^2} = \frac{d^2Y}{dX^2}\left(\frac{dX}{dT}\right)^2 \qquad \text{(since } \frac{d^2X}{dT^2} = 0\text{)}$$

Integral YdT:          Not implemented

Integral (Y/T)dT:   Not implemented

DIPPR 115

Equation:
$$Y = \exp\left(A + \frac{B}{T} + C\ln(T) + DT^2 + \frac{E}{T^2}\right)$$

First Derivative:
$$\frac{d(\ln(Y))}{dT} = -\frac{B}{T^2} + \frac{C}{T} + 2DT - \frac{2E}{T^3}$$

$$\frac{dY}{dT} = Y\frac{d(\ln(Y))}{dT}$$

Second Derivative:
$$\frac{d^2(\ln(Y))}{dT^2} = \frac{2B}{T^3} - \frac{C}{T^2} + 2D + \frac{6E}{T^4}$$

$$\frac{d^2Y}{dT^2} = Y\left(\frac{d^2(\ln(Y))}{dT^2} + \left(\frac{d(\ln(Y))}{dT}\right)^2\right)$$

Integral YdT:          Not implemented

Integral (Y/T)dT:   Not implemented

DIPPR 116

Equation:
$$Y = A + BX^{0.35} + CX^{\frac{2}{3}} + DX + EX^{\frac{4}{3}}$$

where $X = 1 - T_r$

First Derivative:
$$\frac{dY}{dX} = 0.35BX^{-0.65} + \frac{2}{3}CX^{-\frac{1}{3}} + D + \frac{4}{3}EX^{\frac{1}{3}}$$

$$\frac{dX}{dT} = -\frac{1}{T_c}$$

$$\frac{dY}{dT} = \frac{dY}{dX}\frac{dX}{dT}$$

Second Derivative:

$$\frac{d^2Y}{dX^2} = -0.2275BX^{-1.65} - \frac{2}{9}CX^{-\frac{4}{3}} + \frac{4}{9}EX^{-\frac{2}{3}}$$

$$\frac{d^2Y}{dT^2} = \frac{d^2Y}{dX^2}\left(\frac{dX}{dT}\right)^2 \qquad \text{(since } \frac{d^2X}{dT^2} = 0\text{)}$$

Integral YdT:          Not implemented

Integral (Y/T)dT:  Not implemented

Notes                      Cannot be evaluated if $X < 0$

# Appendix C. *Supercritical Extrapolation Options*

For any of the DIPPR equations the user can choose to use an extrapolation method when the temperature is greater than the critical temperature (or a specified fraction thereof) called $T_x$ in the equations below. Four possible extrapolation options are available.

**Constant value above $T_x$**

$$Y = Y_{Tx}$$

$$\frac{dY}{dT} = 0$$

$$\frac{d\ln(Y)}{dT} = 0$$

$$\frac{d^2Y}{dT^2} = 0$$

$$\frac{d^2\ln(Y)}{dT^2} = 0$$

**Constant First Derivative above $T_x$**

$$Y = Y_{Tx} + (T - T_x)\left(\frac{dY}{dT}\right)_{Tx}$$

$$\frac{dY}{dT} = \left(\frac{dY}{dT}\right)_{Tx}$$

$$\frac{d\ln(Y)}{dT} = \frac{1}{Y}\left(\frac{dY}{dT}\right)$$

$$\frac{d^2Y}{dT^2} = 0$$

$$\frac{d^2\ln(Y)}{dT^2} = 0$$

**Constant Second Derivative above $T_x$**

$$Y = Y_{Tx} + (T - T_x)\left(\left(\frac{dY}{dT}\right)_{Tx} + \frac{1}{2}(T - T_x)\left(\frac{d^2Y}{dT^2}\right)_{Tx}\right)$$

$$\frac{dY}{dT} = (T - T_x)\left(\frac{d^2Y}{dT^2}\right)_{Tx} + \left(\frac{dY}{dT}\right)_{Tx}$$

$$\frac{d\ln(Y)}{dT} = \frac{1}{Y}\left(\frac{dY}{dT}\right)$$

$$\frac{d^2Y}{dT^2} = \left(\frac{d^2Y}{dT^2}\right)_{Tx}$$

$$\frac{d^2\ln(Y)}{dT^2} = \frac{1}{Y}\frac{d^2Y}{dT^2} - \left(\frac{d\ln(Y)}{dT}\right)^2$$

**DNV Supercritical Extrapolation Option**

Unlike the other options this works by computing a modified temperature and using this in the standard DIPPR equation.

The modified temperature is given by:

$$T_{mod} = T\left(1 - \left(\frac{T - T_x}{T}\right)^2\right)$$

When the modified temperature is passed into the standard equation functions, the returned values computed will be for $\dfrac{dY}{dT_{mod}}$ , $\dfrac{d^2Y}{dT^2_{mod}}$ etc. from which we need to calculate $\dfrac{dY}{dT}$ , $\dfrac{d^2Y}{dT^2}$ etc. This can be accomplished from the knowledge that

$$T_{mod} = T - \frac{(T - T_x)^2}{T}$$

$$\frac{dT_{mod}}{dT} = 1 - \frac{1}{T^2}\left(2T(T - T_x) - (T - T_x)^2\right)$$

Which when simplified gives

$$\frac{dT_{mod}}{dT} = \frac{T_x^2}{T^2}$$

And the second differential

$$\frac{d^2T_{mod}}{dT^2} = -2\frac{T_x^2}{T^3}$$

First Derivative

$$\frac{dY}{dT} = \frac{dY}{dT_{mod}}\frac{dT_{mod}}{dT} = \frac{T_x^2}{T^2}\frac{dY}{dT_{mod}}$$

First Log Derivative

$$\frac{d(\ln Y)}{dT} = \frac{1}{Y}\frac{dY}{dT} = \frac{1}{Y}\frac{dY}{dT_{mod}}\frac{dT_{mod}}{dT} = \frac{T_x^2}{T^2}\frac{d(\ln Y)}{dT_{mod}}$$

Second Derivative

$$\frac{d^2Y}{dT^2} = \frac{d^2Y}{dT_{mod}^2}\left(\frac{dT_{mod}}{dT}\right)^2 + \frac{dY}{dT_{mod}}\frac{d^2T_{mod}}{dT^2}$$

So

$$\frac{d^2Y}{dT^2} = \frac{T_x^2}{T^2}\left(\frac{T_x^2}{T^2}\frac{d^2Y}{dT_{mod}^2} - \frac{2}{T}\frac{dY}{dT_{mod}}\right)$$

Second Log Derivative

$$\frac{d^2\ln Y}{dT^2} = \frac{1}{Y}\frac{d^2Y}{dT^2} - \frac{1}{Y^2}\frac{dY}{dT}$$

So

$$\frac{d^2\ln Y}{dT^2} = \frac{1}{Y}\frac{T_x^2}{T^2}\left(\frac{T_x^2}{T^2}\frac{d^2Y}{dT_{mod}^2} - \frac{2}{T}\frac{dY}{dT_{mod}}\right) - \frac{1}{Y^2}\frac{dY}{dT_{mod}}\frac{T_x^2}{T^2}$$

$$\frac{d^2\ln Y}{dT^2} = \frac{1}{Y}\frac{T_x^2}{T^2}\left(\frac{T_x^2}{T^2}\frac{d^2Y}{dT_{mod}^2} - \frac{2}{T}\frac{dY}{dT_{mod}} - \frac{1}{Y}\frac{dY}{dT_{mod}}\right)$$

$$\frac{d^2\ln Y}{dT^2} = \frac{1}{Y}\frac{T_x^2}{T^2}\left(\frac{T_x^2}{T^2}\frac{d^2Y}{dT_{mod}^2} - \left(\frac{2}{T} + \frac{1}{Y}\right)\frac{dY}{dT_{mod}}\right)$$

# Appendix D. *Derivatives and integrals for ideal mixing rules*

Available mixing rules for calculating simple properties for a mixture have been described in Section 3.2.1 Currently implemented are the ideal-mixing rule and the Le Chatelier's mixing rule.

This Appendix includes expressions for derivatives and integrals of the mixing rules, which are required when applying these rules to consequence models. Appendix D.1 includes the equations for a general mixing rule, Appendix D.2 to the ideal-mixing rule, and Appendix D.3 for the Le Chatelier's mixing rule.

In this appendix the following notation is adopted:

- $x_i$ (i=1,…N) are individual mole fractions and $Y_i$ the individual property
- $Y_{mix}$ is the mixture property to be obtained via a mixing rule

## *D.1* Simple Mixing Rules

The simple mixing rules can all be written in a generic form as:

$$Y_{mix} = f(x_i, Y_i)$$

From this, the following relationships follow:

$$\frac{dY_{mix}}{dT} = \frac{d[f(x_i, Y_i)]}{dT}$$

$$\frac{d^2 Y_{mix}}{dT^2} = \frac{d^2[f(x_i, Y_i)]}{dT^2}$$

$$\ln(Y_{mix}) = \ln(f(x_i, Y_i))$$

$$\frac{d[\ln(Y_{mix})]}{dT} = \frac{1}{Y_{mix}} \frac{dY_{mix}}{dT}$$

$$\frac{d^2[\ln(Y_{mix})]}{dT^2} = \frac{1}{Y_{mix}} \frac{d^2 Y_{mix}}{dT^2} - \left( \frac{d[\ln(Y_{mix})]}{dT} \right)^2$$

$$\int Y_{mix} dT = \int f(x_i, Y_i) dT$$

$$\int \frac{Y_{mix}}{T} dT = \int \frac{f(x_i, Y_i)}{T} dT$$

## *D.2* Ideal Mixing

$$Y_{mix} = \frac{\sum [x_i Y_i]}{\sum x_i}$$

$$\frac{dY_{mix}}{dT} = \frac{\sum \left[ x_i \frac{dY_i}{dT} \right]}{\sum x_i}$$

$$\frac{d^2 Y_{mix}}{dT^2} = \frac{\sum \left[ x_i \frac{d^2 Y_i}{dT^2} \right]}{\sum x_i}$$

$$\int Y_{mix} dT = \frac{\sum \left[ x_i \int Y_i dT \right]}{\sum x_i}$$

$$\int \frac{Y_{mix}}{T} dT = \frac{\sum \left[ x_i \int \frac{Y_i}{T} dT \right]}{\sum x_i}$$

## D.3 LeChatelier Mixing

$$\frac{1}{Y_{mix}} = \frac{\sum \frac{x_i}{Y_i}}{\sum x_i}$$

By substituting $Z_i = \frac{1}{Y_i}$ and $Z_{mix} = \frac{1}{Y_{mix}}$

$$\frac{dY_{mix}}{dT} = -\frac{1}{Z_{mix}^2} \frac{dZ_{mix}}{dT}$$

$$\frac{d^2 Y_{mix}}{dT^2} = \frac{1}{Z_{mix}^2} \left[ \frac{2}{Z_{mix}} \left( \frac{dZ_{mix}}{dT} \right)^2 - \frac{d^2 Z_{mix}}{dT^2} \right]$$

Where

$$Z_{mix} = \frac{\sum [x_i Z_i]}{\sum x_i}$$

$$\frac{dZ_{mix}}{dT} = \frac{\sum \left[ x_i \frac{dZ_i}{dT} \right]}{\sum x_i}$$

$$\frac{d^2 Z_{mix}}{dT^2} = \frac{\sum \left[ x_i \frac{d^2 Z_i}{dT^2} \right]}{\sum x_i}$$

And

$$\frac{dZ_i}{dT} = -\frac{1}{Y_i^2} \frac{dY_i}{dT}$$

$$\frac{d^2 Z_i}{dT^2} = \frac{1}{Y_i^2} \left[ \frac{2}{Y_i} \left( \frac{dY_i}{dT} \right)^2 - \frac{d^2 Y_i}{dT^2} \right]$$

# Appendix E.  *Solution method for cubic equations of state*

To determine the condition of the material at a given temperature *T* and pressure *P*, the program must iterate to solve the equation of state.

## E.1   Evaluating Real and Complex Roots

The equation of state expresses compressibility as a cubic of the generalised form:

$$z^3 + bz^2 + cz + d = 0$$

( 169 )

The substitution z = x – b/3 transforms this into 'depressed' form:

$$x^3 + px + q = 0$$

( 170 )

Where p and q are given by:

$$p = \frac{3c - b^2}{3}$$

$$q = \frac{27d - 9bc + 2b^2}{27}$$

( 171 )

If we then substitute x = y – p/3y we get

$$y^3 - \frac{p^3}{(3y)^3} + q = 0$$

( 172 )

This can be expressed as a quadratic in $y^3$ by multiplying through:

$$\left(y^3\right)^2 + q\left(y^3\right) - \left(\frac{p}{3}\right)^3 = 0$$

( 173 )

We can determine if this has real solutions by evaluating R such that:

$$R = \frac{p^3}{27} + \frac{q^2}{4}$$

( 174 )

If R < 0 there are 3 real, unequal roots (i.e. the equation goes through both a maximum and a minimum).  These can be calculated using the logic given in Perry.

If R = 0 there are 3 real roots, at least two of which are equal (i.e. the equation goes though one minimum or maximum and a point of inflexion). Again the Perry logic can be used.

When R > 0 the roots of the quadratic in $y^3$ are complex, and hence 1 real root and two imaginary roots for the cubic in y. The roots of the cubic in y are then[31]:

---

[31] DOC I don't follow how we obtain the cubic roots from the quadratic.

$$y_1 = A + B \tag{175}$$

$$y_2 = -\frac{1}{2}(A + B) + i\frac{\sqrt{3}}{2}(A - B)$$

$$y_3 = -\frac{1}{2}(A + B) - i\frac{\sqrt{3}}{2}(A - B)$$

Where

$$A = (-\frac{q}{2} + \sqrt{R})^{1/3} \tag{176}$$

$$B = (-\frac{q}{2} - \sqrt{R})^{1/3}$$

## E.2   Interpreting Real and Complex Roots

Where there are 3 real roots, the minimum $z_1$ is the liquid compressibility, and the maximum $z_3$ is the vapour compressibility. This applies in both property systems.  However, the more difficult case is where there is a single real root.

Physically, such a solution will typically occur at conditions where either vapour or liquid phase does not exist.  In the new property system (and the MC extension in the old property system) the approach is to use the single real root regardless of whether a liquid or vapour property is requested.  Thus the 'wrong' compressibility might be used for the requested property, but in general clients of the property system models should check whether calls are appropriate (*e.g.* for supercritical conditions).

The old property system takes a different approach[32].  The real parts of the complex roots are used, giving 3 roots, 2 of which are equal:

$$y_1 = A + B \tag{177}$$

$$y_3 = y_2 = -0.5(A + B)$$

To match the roots to a particular phase, they are sorted into ascending order in ZCUBIC so that $y_1$ is liquid and $y_3$ vapour. From above:

$$y_3 - y_1 = y_2 - y_1 = -\frac{3}{2}(A + B) \tag{178}$$

When these are transformed back to z, and assuming SRK where b = -1:

$$z_2 - z_1 = -\frac{3}{2}\left(z_1 - \frac{1}{3}\right) \tag{179}$$

This will only be positive where $z_1 < 1/3$, which is a very small region in the vicinity of the critical point. However, when this occurs the sorting of the roots into ascending order will result in the imaginary root becoming the vapour root.  At all other times in the supercritical region the imaginary root would be returned as the liquid root – which was irrelevant to the old property system because it did not use cubic equations of state for the liquid properties.  However, the new property system can use equation of state methods for the liquid properties, and this situation would be unacceptable because, instead of converging at the critical point the two compressibilities would cross-over.

## E.3   Implication for Property Calculations

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[32] VI4291.

This difference in approach is the basis of the difference in many properties (particularly saturation or dependent properties calculated for mixtures) between the two systems[33]. In part, this is a consequence of attempting to derive 'saturated' properties for a material.

Saturation pressure is taken as the ideal bubble point [sum of $x_iP_{sat}(T)$] of the material. Now, for a pure component this is OK because the bubble point is the same as the dew point, and the ideal bubble point should be close to that which SRK would give. But for a mixture, the bubble point pressure can be very much greater than the dew point pressure, and therefore frequently puts the SRK equation into a region where there is no vapour root. The old property system will estimate this root by using a complex vapour root; the new system will return the only real, liquid, root.

So which approach is better? The answer is neither: the old property system returns values that have no physical significance. The new property system returns values that do have a physical significance, but the wrong one for the requested property. But this is in part caused by the calculating these properties at the bubble point pressure, which for mixtures can be so far removed from the real region in which vapour exists that there is no valid way of calculating vapour properties at all.

Consider liquid enthalpy. In the old property system the main equations used in calculating this property are:

$$P_{but} = \sum x(i)P_{sat}(i) \tag{180}$$

$$H_L[T, P_{bub}] = H_V[T, P_{bub}] - \Delta H_{vap} \tag{181}$$

$$\Delta H_{vap} = T(V_V[T, P_{bub}] - V_{Lsat}[T])\frac{dP_{bub}}{dT} \tag{182}$$

$$H_L[T, P] = H_L[T, P_{bub}] + \left(P - P_{bub}\right)\left(V_{Lsat}[T] - T\frac{dV_{Lsat}}{dT}\right) \tag{183}$$

The main reason that this gives problems (especially for mixtures) is that the use of $P_{bub}$ the calculation of $H_V[T,P_{bub}]$ in ( 181 ) and in the calculation of $V_V[T,P_{sat}]$ in ( 182 ) can push the equation of state into a region where there is a single root which actually belongs to the liquid phase. This is because for a wide boiling mixture the bubble point pressure is very much greater than the dew point pressure which physically is the highest pressure at which vapour can exist.

This error[34] probably came about because the bubble point pressure is used in the flash algorithm as the equivalent of the boiling pressure for a pure component, and the need was to calculate the thermodynamic properties at this pressure for both the liquid and vapour phases. However, it means that for mixtures containing light gases (e.g. Nitrogen, Hydrogen), the pressure used may be very high resulting in failures in the calculation routines.

One alternative approach for improving these methods for mixtures would be to use the ideal dew point rather than bubble point, where vapour roots would be more likely to exist:

$$\frac{1}{P_{dew}} = \sum \frac{x(i)}{P_{sat}(i)} \tag{184}$$

For pure components $P_{bub} = P_{dew} = P_{sat}$ and results should be equal. For multicomponents results would be different, but as the current approach is wrongly implemented (specifically the calculation of $dP_{sat}/dT$ in $\Delta H_{vap}$ – see that property) and should be fixed, this need not be a major impediment.

In any case, saturated properties should never be used in new development. Any "client" application should instead make the standard property call with both T and P specified. This still leaves properties such as liquid enthalpy where these properties are used directly. In this case, eventually the preferred 'template' set of property methods should be used, where properties such as these are derived from the equation of state.

## E.4    Solution of Soave-Redlich-Kwong Equation

The Soave-Redlich-Kwong equation can be expressed as function f(Z) of the compressibility *Z* as follows:

$$f = Z^3 - Z^2 + CZ - D \tag{185}$$

---

[33] ERROR. This is a complex issue, and is documented in more detail in VI6412.

[34] VI6414

$$C = A^2 P - BP(1 + BP)$$

$$D = \left(A^2 P\right)\left(BP\right)$$ **( 186 )**

$$A^2 = \frac{a\alpha}{T^2}$$ **( 187 )**

$$B = \frac{\overline{b}}{T}$$ **( 188 )**

$$f' = 3Z^2 - 2Z + C$$ **( 189 )**

$$f'' = 6Z - 2$$ **( 189 )**

See Section 3 for a full description of the equation of state and its constants.
Note:

$$A^2 P > 0$$
$$BP > 0$$
$$f(0) = -D$$

Properties of the function

$f(0) = -D < 0$.
$f''(1/3) = 0$ and $f''$ is linear ($f''' = 6$).
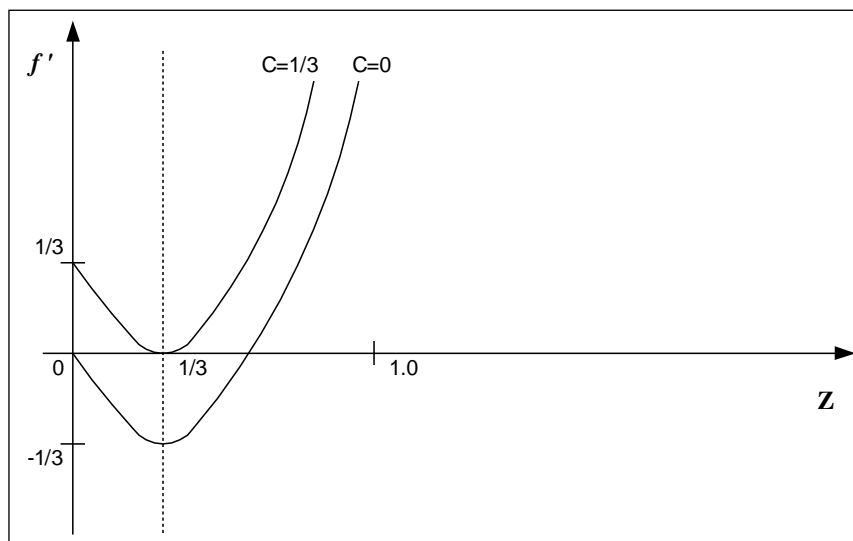$f'(1/3) = C - 1/3$ and $f'$ is a set of parabolas, as shown in
Figure 4.



**Figure 4: Derivative *f'*(Z) to cubic equation f(Z) for Soave-Redlich-Kwong**

The form of *f* for a range of values of *C* are shown in Figure 5.
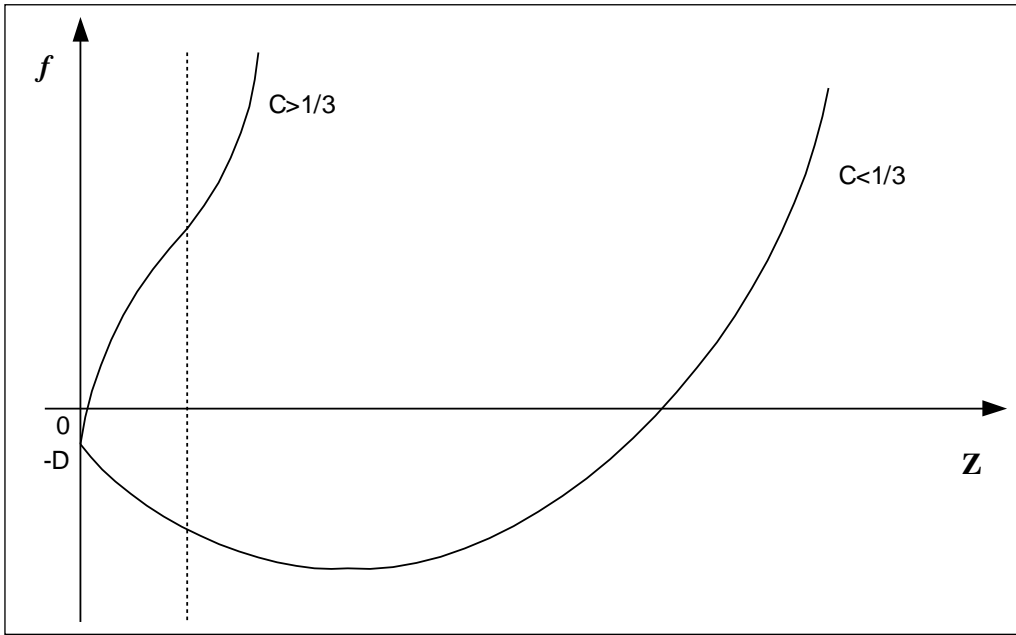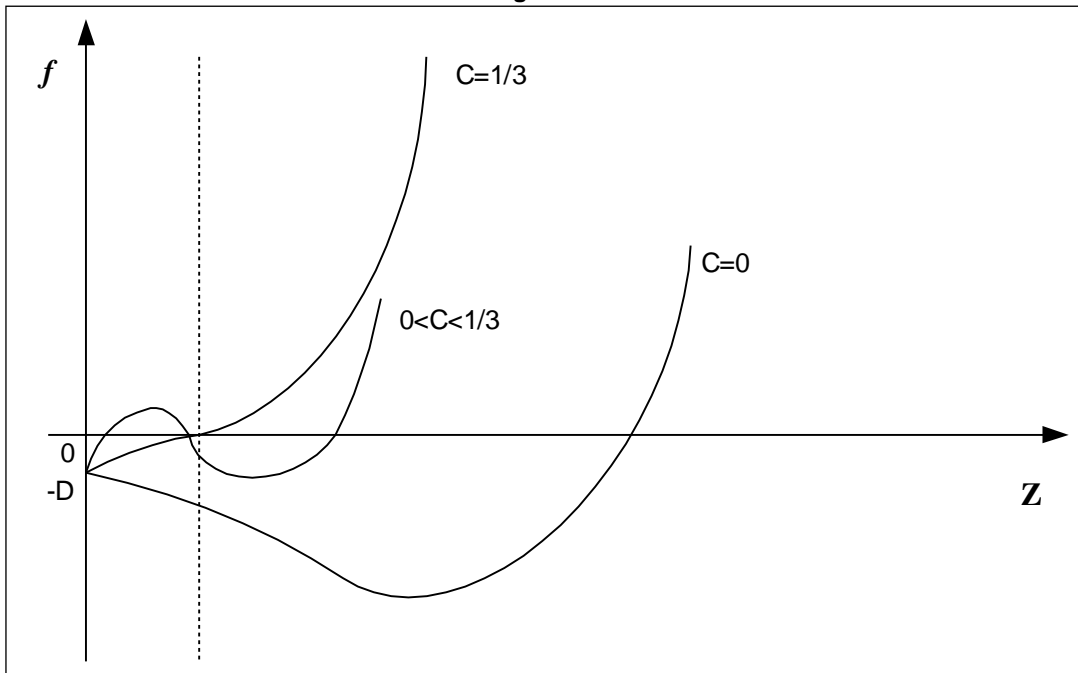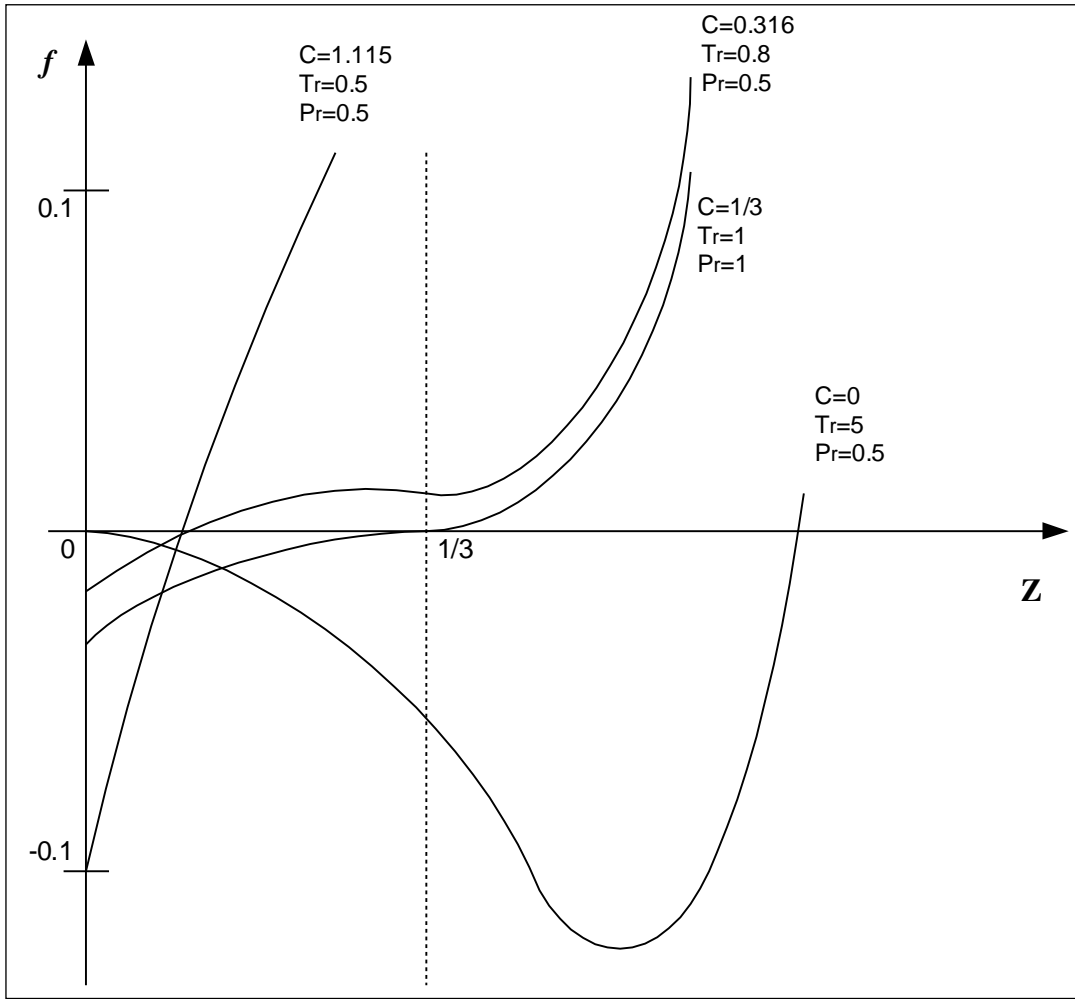
**Figure 5a**



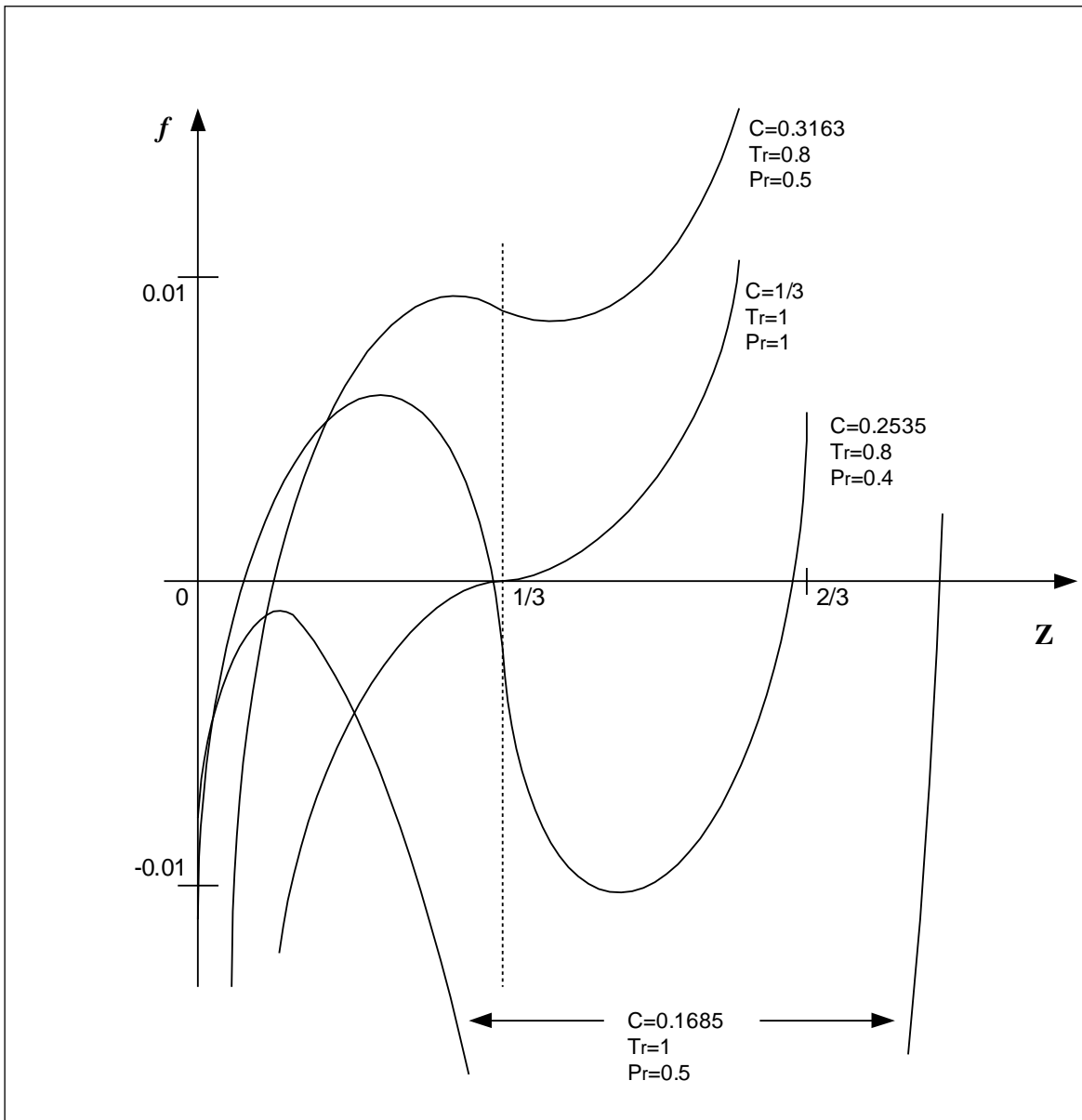**Figure 5b**

**Figure 5c**

**Figure 5d**

**Figure 5: Cubic equation f(Z) for Soave-Redlich-Kwong**

An iteration is performed to obtain the positive value (or values) of $z$ such that $f(z) = 0$. The iteration is performed using Newton's method, with the stages given below.

## Determine if 3 or 1 Real Roots Exist

For 3 real positive roots to exist it is necessary, but not sufficient, that $f(z)$ reaches a maximum and a minimum for $z > 0$.

Setting $f'=0$ and solving for $Z_{max}$ and $Z_{min}$ gives:

$$Z_{min} = \tfrac{1}{3} + \sqrt{\tfrac{1}{9} - \tfrac{1}{3}C}$$

$$Z_{max} = \tfrac{1}{3} - \sqrt{\tfrac{1}{9} - \tfrac{1}{3}C}$$

Thus $C$ must be $\leq 1/3$ for $Z_{min}$ and $Z_{max}$ to have real values and $C$ must be positive for the maximum value to occur at a positive value of $Z$ (because $f(0)= -D$ and $D>0$).

- $c > 1/3$
  Neither $Z_{max}$ or $Z_{min}$ exist and only 1 real root exists.

- $c \leq 0$
  $Z_{min}$ exists but $Z_{max} > 0$ does not so three real positive roots do not exist.

- $0 < c \leq 1/3$
  3 real positive roots may exist.

Three positive unequal roots exist if:

$$\frac{b_1^2}{4} + \frac{a^3}{27} < 0$$

where:

$$a = f'(1/3) = C - \frac{1}{3}$$

$$b_1 = f(1/3) = \frac{1}{3}C - D - \frac{2}{27}$$

Otherwise only 1 real root exists.

## To Find the Vapour Root

*Three Positive Roots Exist*

The program uses Newton's method starting with a large value for $Z$, e.g. $Z_o=1.5$. The program requires any value for $Z$ used in the iteration to satisfy $f'(Z)> 0$ to prevent locating the spurious middle root.

*One Positive Root Exists*

The program uses Newton's method to locate the root.

If $b_1 > 0$, let $Z_0 = Z_{LB} = BP$.
If $b_1 < 0$, let $Z_0 = 3.0$
$f'(Z)> 0$ is required.
If $Z_{min}$ does not exist ($a \geq 0$) accept the root found as a vapour root.
If $Z_{min}$ exists ($a < 0$) compare the root found to $Z_{min}$. If $Z \geq Z_{min}$ accept the root as a proper vapour root. If $Z < Z_{min}$ reject the root found and set $Z = Z_{min}$.

## To find the Liquid Root

*Three Positive Roots Exist*

The program uses Newton's method starting with a large value for $Z$, e.g. $Z_0=1.5$. The program requires any value for $Z$ used in the iteration to satisfy $f'(Z) > 0$ to prevent locating the spurious middle root.

*One Positive Root Exists*

The program uses Newton's method to locate the root.

If $b_1 > 0$, let $Z_0 = Z_{LB} = BP$.
If $b_1 < 0$, let $Z_0 = 3.0$
$f'(Z) > 0$ is required.
If $Z_{max}$ exists ($C > 0$) compare the root found to $Z_{max}$. If $Z \leq Z_{max}$ accept the root as a proper liquid root. If $Z > Z_{max}$ reject the root found and set $Z = Z_{max}$.

## Selection of the Lower Bound ($Z_{LB}$)

$f(0) = -D$ which is negative so $Z_{LB} = 0$ is a lower bound. However, subsequent calculations require evaluation of $\ln(Z-BP)$ so if $BP$ is a greater lower bound, $Z_{LB} = BP$ would be preferable.

Evaluating $f(Z)$ on the interval $0 < Z \leq BP$.

$$\text{Let } z = x\overline{BP} \quad 0 < x \leq 1$$
$$f\left(x\overline{BP}\right) = x^3\overline{BP}^3 - x^2\overline{BP}^2 + C\overline{BP} - D$$
$$C = \overline{A^2P} - \overline{BP}\left(1 + \overline{BP}\right) \quad D = \overline{A^2P}\,\overline{BP}$$
$$= \frac{D}{\overline{BP}} - \overline{BP}\left(1 + \overline{BP}\right)$$
$$f\left(x\overline{BP}\right) = x^3\overline{BP}^3 - x^2\overline{BP}^2 + \left(D - \overline{BP}^2 - \overline{BP}^3\right)x - D$$
$$= \left(x^3 - x\right)\overline{BP}^3 - \left(x^2 + x\right)\overline{BP}^2 - (1\text{-}x)$$
$$x^3 - x \leq 0 \quad 0 < x \leq 1$$
$$-\left(x^2 + x\right) < 0 \quad 0 < x \leq 1$$
$$-(1 - x) \leq 0 \quad 0 < x \leq 1$$
$$\text{so } f\left(x\overline{BP}\right) < 0 \quad 0 < x \leq 1$$

Therefore $BP$ can be used for $Z_{LB}$.

## Selection of Starting Point for Newton Iteration

- *$f'' < 0$ in vicinity of root, $Z_{ROOT}$*
  Start $Z_0$ on the side of $Z_{ROOT}$ where $f$ and $f'$ have opposite sign.

- *$f'' > 0$ in vicinity of root, $z_{ROOT}$*
  Start $Z_0$ on the side of $Z_{ROOT}$ where $f$ and $f'$ have the same sign.

If the signs of $f'$ and $f''$ do not change on the interval $Z_0$-$Z_{ROOT}$ the procedure will converge, unless $|f'|$ becomes too small.

## E.5 Solution of Peng-Robinson Equation

The Peng-Robinson equation can be expressed in terms of the compressibility $Z$ as follows:

$$f = Z^3 - bZ^2 + CZ - D \qquad (190)$$

$$b = 1 - \overline{BP}$$

$$C = A^2 P - \overline{BP}(2 + 3\overline{BP})$$

$$D = \overline{BP}\left[A^2 P - \overline{BP}(1 + \overline{BP})\right]$$

$$A^2 = \frac{\overline{a\alpha}}{T^2} \qquad (191)$$

$$B = \frac{\overline{b}}{T} \qquad (192)$$

$$f' = 3Z^2 - 2bZ + C \qquad (193)$$

$$f'' = 6Z - 2b \qquad (194)$$

$$f''' = 6 \qquad (195)$$

See Section 3 for a full description of the equation of state and its constants.

Note:

$$A^2 P > 0$$

$$BP > 0$$

$$f(0) = -D$$

$$f''\left(\frac{b}{3}\right) = 0$$

This is a cubic equation similar to the Soave-Redlich-Kwong equation but slightly more complicated.

## **Properties of the function**

The inflection point is at $f''(Z_{in}) = 0$, where $Z_{in} = b/3$.
For a maximum and minimum to exist for positive values of $Z$, set $f' = 0$ solve for $Z_m$:

$$Z_m = \frac{b}{3} \pm \sqrt{\left(\frac{b}{3}\right)^2 - \frac{C}{3}}$$

Thus for 3 positive real roots to exist, $C$ must be in the range $0 < C \le b^2/3$.

## **Selection of the Lower Bound ($Z_{LB}$)**

$f(0) = -D$ which is negative so $Z_{LB} = 0$ is a lower bound. However, subsequent calculations require evaluation of $\ln(Z-BP)$ so if $BP$ is a greater lower bound, $Z_{LB} = BP$ would be preferable.

Evaluating $f(Z)$ on the interval $0 < Z \le BP$.

Let $z = x\overline{BP} \quad 0 < x \le 1$

$$f\left(x\overline{BP}\right) = x^3 \overline{BP}^3 - \left(1 - \overline{BP}\right)x^2 \overline{BP}^2 + \left[A^2 P - \overline{BP}(2 + 3\overline{BP})\right]x\overline{BP} - D$$

$$A^2 P = \frac{D}{\overline{BP}} + \overline{BP}(1 + BP)$$

$$f\left(x\overline{BP}\right) = x^3 \overline{BP}^3 - x^2\left(\overline{BP}^2 - \overline{BP}^3\right) + \left(D - \overline{BP}^2 - 2\overline{BP}^3\right)x - D$$

$$= \left(x^3 - x^2 - 2x\right)\overline{BP}^3 - \left(x^2 + x\right)\overline{BP}^2 - (1 - x)D$$

Thus $f\left(x\overline{BP}\right) \le 0$ if $D \ge 0$ $\quad 0 \le x \le 1$

For $D \ge 0$ $\quad A^2 P \ge BP(1 + BP)$

Substituting for $A^2B$ and $BP$ gives:

$$5.877\alpha \ge T_R + 0.0778P_R$$

This restriction must apply or a root exists in the range $0 < Z \le BP$.

**Iterative Procedure to Find the Roots**

*Determine if Three or One Real Roots Exist*

Three real positive roots *may* exist if $0 < C \le b^2/3$.
Three positive unequal roots do exist if:

$$\frac{\beta^2}{4} + \frac{a^3}{27} < 0$$

where:

$$a = f'(b/3) = C - \frac{b^2}{3}$$

$$\beta = f(b/3) = -\frac{2b^2}{27} + \frac{bC}{3} - D$$

Otherwise only 1 real root exists.

*To Find the Vapour Root*

The procedure is the same as for the Soave-Redlich-Kwong equation, described in Section A.2.2.

*To Find the Liquid Root*

The procedure is the same as for the Soave-Redlich-Kwong equation, described in Section A.2.3.

# Appendix F.   Water as a separate phase (not yet made available via XPRP)

## *F.1* Derivation of properties

The multi-phase equilibrium algorithms that can treat the water liquid phase in a rigorous way are relatively rare and it is beyond the scope of this model to perform multi-phase equilibrium calculations involving more than two phases. A simple way to model the water liquid phase is to treat water in hydrocarbon processes as a "separated" component, and this is provided as an option in this model.

**NB**: For PHAST / SAFETI 6.5 there is no such option for the special handling of water in the new property system.  This option did apparently exist in the MC extension to the old property system, and the theory is retained here for potential future inclusion.

When water is treated as a "separated" component, it is assumed throughout that liquid water and the other liquid components (typically hydrocarbons) are insoluble. The properties of water are obtained using the ASME (1967) correlations; the properties of the mixture are calculated as described in Section 3.4, but with the water removed from both the vapour mixture and the liquid mixture. The water properties are then combined back into the total mixture properties, as shown:

*Vapour Enthalpy:*

$$H_v = (1 - y_W)H_{v,HC} + y_W H_{v,W}$$

( 196 )

where:

$y_W$        is the mole fraction of water in the vapour phase
$H_{v,HC}$, $H_{v,W}$    are the vapour enthalpies of hydrocarbon (i.e. the mixture) and of water.

*Liquid Enthalpy:*

$$H_L = (1 - x_W)H_{L,HC} + y_W H_{L,W}$$

( 197 )

where:

$x_W$        is the mole fraction of water in the liquid phase
$H_{L,HC}$, $H_{L,W}$    are the liquid enthalpies of hydrocarbon (i.e. the mixture) and of water.

*Vapour Entropy:*

$$s_v = (1 - y_W)(s_{v,HC} - R\ln(1 - y_W)) + y_W(s_{v,W} - R\ln(y_W))$$

( 198 )

where:

$s_{v,HC}$, $s_{v,W}$    are the vapour entropies of hydrocarbon (i.e. the mixture) and of water.

*Liquid Entropy:*

$$s_L = (1 - x_W)s_{L,HC} + x_W s_{L,W}$$

( 199 )

where:

$s_{L,HC}$, $s_{L,W}$    are the liquid entropies of hydrocarbon (i.e. the mixture) and of water.

*Vapour Density:*

$$\rho_v = \frac{1}{V_v}$$

( 200 )

$$V_v = \frac{(1 - y_W)}{\rho_{v,HC}} + \frac{y_W}{\rho_{v,W}}$$

( 201 )

$\rho_{v,HC}$, $\rho_{v,W}$ are the vapour densities of hydrocarbon (i.e. the mixture) and of water.

*Liquid Density:*

$$\rho_L = \frac{1}{V_L}$$

( 202 )

$$V_L = \frac{(1 - x_W)}{\rho_{L,HC}} + \frac{x_W}{\rho_{L,W}}$$

( 203 )

$\rho_{L,HC}$, $\rho_{L,W}$ are the liquid densities of hydrocarbon (i.e. the mixture) and of water.

### ASME Correlations for water properties

The new multi-compound property system also includes water properties obtained by means of AMSE steam tables. The properties are documented in detail by pages 13-48 in the ASME Steam Tables, and the reader is referred to any further details to this document.[35]

## *F.2* Modelling phase equilibrium

The multi-phase equilibrium algorithms that can treat the water liquid phase in a rigorous way are relatively rare and it is beyond the scope of this model to perform multi-phase equilibrium calculations involving more than two phases. A simple way to model the water liquid phase is to treat water in hydrocarbon processes as a "separated" component, and this is provided as an option in this model.

The following assumptions are made when the separated water option is chosen:

1. Liquid water and liquid hydrocarbon form two immiscible phases.

2. Water in the vapour phase follows the Lewis and Randall Rule.

3. The effect of pressure on the pure component vapour and liquid fugacities of water cancels in the calculation of the water *K*-value. Then the partial pressure of water equals its vapour pressure.

The *K*-values that apply to the overall vapour and liquid phases containing water are obtained as follows:

1. Calculate the compositions of the vapour and liquid phases on a water-free basis.

2. Calculate the K-values $K_{HC,i}$ for all components except water at total system pressure and temperature and using the water free compositions.

3. Calculate the vapour pressure of water.

4. Obtain the K-values to be used with the original total mole fractions:

$$K_W = \frac{p_W^s}{x_W P}$$

( 204 )

$$K_i = \frac{K_{HC,i}}{(1 - x_W)}$$

( 205 )

where *i* is any component except water

# Appendix G. Details of solution method (isothermal or constant vapour fraction flash)

This vapour-liquid equilibrium calculation is used when *P&Ψ* or *T&Ψ* or *P&T* are known. The algorithm finds the third unknown parameter (*T, P* or *Ψ*) and the equilibrium compositions.

After solving the equations and determining equilibrium flash conditions, the program calculates *H, s, M and ρ* (density) for each phase and for the total fluid.

The symbols used are described at the end of the appendix.

## *G.1* Flash Equations

The main phase equilibrium equation is given as Equation ( 151 ) and the material balance equations are given as Equations ( 152 ) to ( 155 ).

From these equations, $D_i$ is defined as:

$$D_i = \Psi K_i + 1 - \Psi \quad \{i = 1, NC\}$$

( 206 )

and the liquid fractions {$x_i$} and vapour fractions {$y_i$} can be calculated from the equations:

$$x_i = z_i / Di \qquad \{i = 1, NC\}$$

( 207 )

$$y_i = K_i x_i \qquad \{i = 1, NC\}$$

( 208 )

## **P&Ψ are specified and T is sought**

The program sets:

$$K_i = K_i^* P_{i,sat}$$

( 209 )

where:

$$K_i^* = K_i^* \left(T, P, \mathbf{y}, \mathbf{x}\right)$$

When $K_i^*$ is held fixed, then:

$$\left(\frac{\partial K_i}{\partial T}\right)_{K_i^* P, \Psi} = K_i^*\left(\frac{dP_{i,sat}}{dT}\right) = \frac{K_i}{P_{i,sat}}\left(\frac{dP_{i,sat}}{dT}\right) = K_i\left(\frac{d \ln P_{i,sat}}{dT}\right)$$

( 210 )

## **T&Ψ are specified and P is sought**

The program sets:

$$K_i = \frac{K_i^*}{P}$$

( 211 )

Then:

$$\left(\frac{\partial K_i}{\partial P}\right)_{K_i^* T, \Psi} = -\left(\frac{K_i^*}{P^2}\right) = -\frac{K_i}{P} \qquad (\,212\,)$$

## P&T are specified and Ψ is sought

The program sets:

$$K_i = K_i^* \qquad (\,213\,)$$

Then:

$$\left(\frac{\partial K_i}{\partial \Psi}\right)_{K_i^* P, T} = 0 \qquad (\,214\,)$$

## G.2    Outer Loop Iterative Procedure For {$K_i$ *}

1.   We get an initial estimate the K-values from the Raoult law:
2.

$$K_{i,0} = \frac{P_{i,sat}}{P} \qquad (\,215\,)$$

then:

$$K_{io}{}^* = 1/P \qquad \text{if T is sought}$$

$$K_{io}{}^* = P_{i,sat} \qquad \text{if P is sought}$$

$$K_{io}{}^* = K_{io} \qquad \text{if } \Psi \text{ is sought}$$

3.   We converge the inner loop (described in Sections G.3, G.4, G.5) to get value of T, P or $\Psi$ resulting from $\{K_i{}^*\}_m$

If $\Psi$ was set to 0 or to 1 in step 2 we recalculate $y_i \ \& \ x_i$.

3.   We calculate:
4.

$$\left\{K_i^*\right\}_{m+1} = K_i^*(T_m, P_m, \mathbf{y}_m, \mathbf{x_m})$$

5.   We iterate steps 2 & 3 until convergence.

*Convergence tests:*

$$\left| \ [\Psi y_i + (1-\Psi)x_i - z_i]_m \ \right| \leq TOLC_i \ i = 1, NC$$

where

$$TOLC_i = \text{Max}(0.0001\, z_i \,, 10^{-9})$$

$$\text{and} \qquad \left| \ T_m - T_{m-1} \ \right| \ \leq \ 0.005$$

$$\text{or} \qquad \left| \ 1 - P_{m-1}/P_m \ \right| \ \leq \ 0.0001$$

$$\text{or} \qquad \left| \ \Psi_m - \Psi_{m-1} \ \right| \ \leq \ 0.00002$$

$$\text{and} \qquad \left| \ G_m \ \right| \ \leq \ 0.0001 \ [\text{using } \{K_i{}^*\}_{m+1}]$$

$G_m$ is not tested if $\Psi_m$ has not been set to 0 or 1.

## G.3 Inner loop iteration when P&Ψ are specified and T is sought

A variable transformation is used to improve the convergence characteristics of the algorithm. If $u$ is set to *1/T:*

$$u = \frac{1}{T}$$

Then the following equations can be derived:

$$G = \ln\left(\frac{\sum_i y_i}{\sum_i x_i}\right) = f(u)$$

$$\frac{dG}{dT} = \frac{\sum_i x_i}{\sum_i y_i}\left\{\frac{\left(\sum_i x_i\right)\dfrac{d\sum_i y_i}{dT} - \left(\sum y_i\right)\dfrac{d\sum x_i}{dT}}{\left(\sum_i x_i\right)^2}\right\}$$

$$du = -\frac{1}{T^2}\,dT$$

$$\frac{dG}{du} = -T^2\left(\frac{dG}{dT}\right)$$

$$\frac{d\sum_i y_i}{dT} = \sum_i \frac{dy_i}{dT}$$

$$\frac{d\sum_i x_i}{dT} = \sum_i \frac{dx_i}{dT}$$

$$\left(\frac{\partial y_i}{\partial T}\right)_{K_i^*,P,\Psi} = \left(\frac{\partial K_i}{\partial T}\right)_{K_i^*,P,\Psi} x_i + K_i\left(\frac{\partial x_i}{\partial T}\right)_{K_i^*,P,\Psi}$$

$$\left(\frac{\partial x_i}{\partial T}\right)_{K_i^*,P,\Psi} = -\frac{z_i}{D_i^2}\left(\frac{\partial D_i}{\partial T}\right)_{K_i^*,P,\Psi} = -\Psi\frac{x_i}{D_i}\left(\frac{\partial K_i}{\partial T}\right)_{K_i^*,P,\Psi}$$

$$= -\Psi\frac{x_i K_i}{D_i}\left(\frac{d\ln p_i^s}{dT}\right) = -\Psi\frac{y_i}{D_i}\left(\frac{d\ln p_i^s}{dT}\right)$$

$$\left(\frac{\partial y_i}{\partial T}\right)_{K_i^*,P,\Psi} = \left(\frac{d\ln p_i^s}{dT}\right) K_i\left[x_i - \frac{\Psi y_i}{D_i}\right]$$

$$= \left( \frac{d \ln p_i^s}{dT} \right) \frac{K_i}{D_i} \left[ (1-\Psi)x_i \right]$$

$$= - \frac{y_i}{D_i} \left( \frac{d \ln p_i^s}{dT} \right) (\Psi - 1)$$

$$\sum_i \frac{\partial x_i}{\partial T} = -\Psi \sum_i \frac{y_i}{D_i} \frac{d \ln p_i^s}{dT}$$

$$\sum_i \left( \frac{\partial y_i}{\partial T} \right) = -(\Psi - 1) \sum_i \frac{y_i}{D_i} \frac{d \ln p_i^s}{dT}$$

$$\frac{dG}{dT} = \frac{\partial/\partial T \left( \sum_i y_i \right)}{\sum_i y_i} - \frac{\partial/\partial T \left( \sum_i x_i \right)}{\sum_i x_i}$$

$$= \left[ \frac{(1-\Psi)}{\sum_i y_i} + \frac{\Psi}{\sum_i x_i} \right] \sum_i \frac{y_i}{D_i} \frac{d \ln p_i^s}{dT}$$

$$\frac{dG}{du} = -T^2 \left[ \frac{1-\Psi}{\sum_i y_i} + \frac{\Psi}{\sum_i x_i} \right] \sum_i \frac{y_i}{D_i} \left( \frac{d \ln p_i^s}{dT} \right) = G'$$

$G'$ < 0 for all T between the upper and lower bound: $T_{LB} \leq T \leq T_{UB}$. Therefore G is monotonic. Then *u* can be determined by a Newton-Raphson iteration:

$$u_{n+1} = u_n - G_n / G'_n$$

One bound can then be set:

If $G_n$ > 0, $T_{LB} = T_n$,
If $G_n$ < 0, $T_{UB} = T_n$

The temperature $T_{n+1} = 1/u_{n+1}$ is constrained within the bounds:

$$T_{LB} < T_{n+1} < T_{UB}$$

Convergence of the inner loop is assumed when:

$$\left| T_{n+1} - T_n \right| < 0.001$$

Then the outer loop temperature is set to the converged inner loop temperature:

$$T_m = T_n$$

## G.4  Inner Loop Iteration when T&$\Psi$ are specified and P is sought

$$G = \sum_i y_i - \sum_i x_i$$

$$G' = \left(\frac{\partial \sum_i y_i}{\partial P}\right)_{K_i^*,T,\Psi} - \left(\frac{\partial \sum_i x_i}{\partial P}\right)_{K_i^*,T,\Psi}$$

$$\left(\frac{\partial x_i}{\partial P}\right)_{K_i^*,T,\Psi} = -\frac{z_i}{D_i^2}\left(\frac{\partial D_i}{\partial P}\right)_{K_i^*,T,\Psi} = \frac{x_i}{D_i}\Psi\left(\frac{\partial K_i}{\partial P}\right)_{K_i^*,T,\Psi}$$

$$= \Psi\frac{x_i}{D_i}\frac{K_i}{P} = \frac{\Psi}{P}\frac{y_i}{D_i}$$

$$\left(\frac{\partial y_i}{\partial P}\right)_{K_i^*,T,\Psi} = x_i\left(\frac{\partial K_i}{\partial P}\right)_{K_i^*,T,\Psi} + K_i\left(\frac{\partial x_i}{\partial P}\right)_{K_i^*,T,\Psi}$$

$$\left(\frac{\partial y_i}{\partial P}\right)_{K_i^*,T,\Psi} = -\frac{y_i}{P}+\frac{K_i\Psi}{P}\frac{y_i}{D_i}=\frac{1}{P}(-\frac{y_i}{D_i})(D_i-K_i\Psi)$$

$$= \frac{(1-\Psi)}{P}\left(-\frac{y_i}{D_i}\right)$$

$$G' = \frac{1}{P}\left(-\sum_i\frac{y_i}{D_i}\right)[1-\Psi+\Psi] = -\frac{1}{P}\sum_i\frac{y_i}{D_i}$$

So $G'$ < 0 for all P > 0 and G decreases monotonically for all positive P as long as:

$$K_i^* > 0 \; and \; 0 \le \Psi \le 1 .$$

Then P can be determined by a Newton-Raphson iteration:

$$P_{n+1} = P_n - G_n/G_n'$$

One bound can be set depending on the sign of $G_n$:

$$G_n > 0 \qquad P_{LB} = P_n$$
$$G_n < 0 \qquad P_{UB} = P_n$$

The pressure $P_{n+1}$ is constrained so that: $P_{LB} < P_{n+1} < P_U$

Convergence is assumed when:

$$\left|1 - P_n/P_{n+1}\right| \le 0.0001$$

Then the outer loop pressure can be set to the inner loop pressure:
$$P_m = P_n$$

## G.5 Inner loop iteration when P & T are specified and $\Psi$ is sought

$$G \quad = \sum_i y_i - \sum_i x_i = \sum_i \frac{(K_i - 1)\,z_i}{D_i}$$

$$G' \quad = \left(\frac{\partial \sum_i y_i}{\partial \Psi}\right)_{K_i^*,P,T} - \left(\frac{\partial \sum_i x_i}{\partial \Psi}\right)_{K_i^*,P,T}$$

$$\left(\frac{\partial x_i}{\partial \Psi}\right)_{K_i^*,P,T} \quad = -\frac{z_i}{D_i^2}\left(\frac{\partial D_i}{\partial \Psi}\right) = -\frac{z_i}{D_i^2}\,(K_i - 1)$$

$$\left(\frac{\partial y_i}{\partial \Psi}\right)_{K_i^*,P,T} \quad = -\frac{K_i z_i}{D_i^2}\left(\frac{\partial D_i}{\partial \Psi}\right) = -\frac{z_i}{D_i^2}\,(K_i - 1)K_i$$

$$\left(\frac{\partial y_i}{\partial \Psi}\right)_{K_i^*,P,T} - \left(\frac{\partial x_i}{\partial \Psi}\right)_{K_i^*,P,T} \quad = -\frac{z_i}{D_i^2}\,(K_i - 1)^2$$

$$G' = -\sum_i \left(\frac{K_i - 1}{D_i^2}\right) z_i < 0 \qquad -\infty < \Psi < \infty$$

$G$ has $NC$ infinite discontinuities in $-\infty < \Psi < \infty$ that occur where the $D_i = 0$ (all $0 \leq z_i \leq 1$).

$$D_{i\infty} = (K_i - 1)\,\Psi_{i\infty} + 1 = 0$$

$$\Psi_{i\infty} = -\left(\frac{1}{K_i - 1}\right)$$
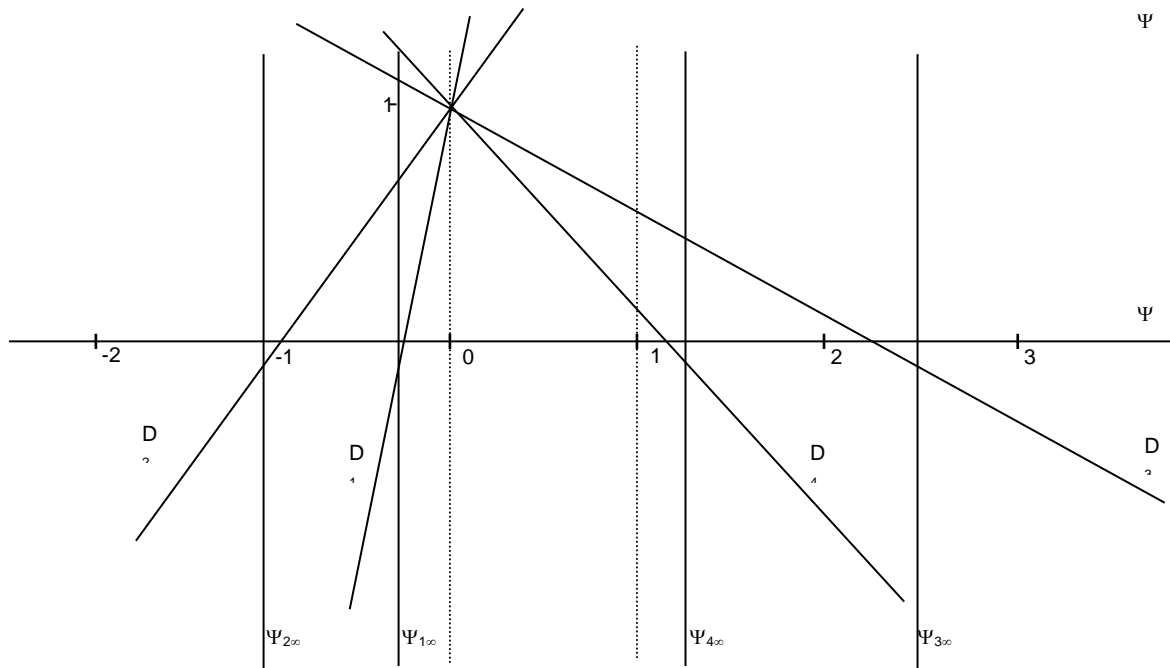
A sketch of the Di for a 4-component case having 2 Ki < 1 and 2 Ki > 1 is shown in Figure 6 and

Figure 6: Representation of the function $Di_\infty$
Representation of the function Di∞ = (Ki-1)Ψi ∞+1 for 4 values of Ki :
K1=5 $\Rightarrow$ Ψ1∞ = -0.25, K2=2 $\Rightarrow$ Ψ2∞ = -1, K3 = 2.5 $\Rightarrow$ Ψ3∞ = 2.5, K4 = 0.2 $\Rightarrow$ Ψ4∞ = 1.25

Figure 7.

**Figure 6: Representation of the function $D_{i\infty}$**
Representation of the function $D_{i\infty} = (K_i-1)\Psi_{i\infty}+1$ for 4 values of $K_i$ :
$K_1=5 \Rightarrow \Psi_{1\infty} = -0.25$, $K_2=2 \Rightarrow \Psi_{2\infty} = -1$, $K_3 = 2.5 \Rightarrow \Psi_{3\infty} = 2.5$, $K_4 = 0.2 \Rightarrow \Psi_{4\infty} = 1.25$
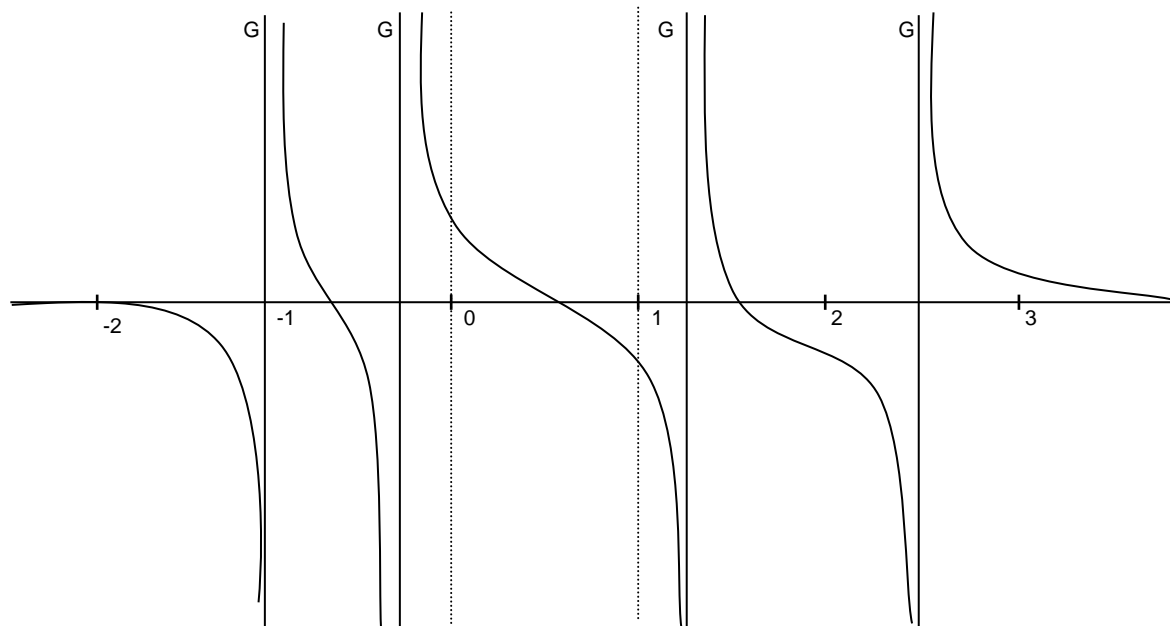


**Figure 7: Illustration of G as a function of the vapour fraction $\Psi$**

The function G is seen to have NC-1 roots. Each root lies between a pair of the $\Psi_{i\infty}$ . Since we restrict $X^i$ and $z_i$ to be $X^i \geq 0$ and $z^i \geq 0$ then we require $D^i > 0$.

Thus, mathematically, we desire to find the root that lies in the interval bounded by:

$$\Psi_{LB} = \text{Max } \Psi_{i\infty} \text{ where } \Psi_{i\infty} < 0 \text{ and}$$

$$\Psi_{UB} = \text{Min } \Psi_{i\infty} \text{ where } \Psi_{i\infty} > 1 \text{ and}$$

$$\Psi_{LB} < \Psi < \Psi_{UB}$$

This keeps all $D_i > 0$

It should be noticed that no $\Psi_{i\infty}$ can lie in the range $0 \leq \Psi_{i\infty} \leq 1$

This is because we require all $K$-values to be positive: $K_i > 0$.

In order to have $\Psi_{i\infty} > 0$ it is required that: $K_i > 1$

If $\Psi_{i\infty} > 1$ then it is required that: $K_i < 1$

Thus if there is not even one $K$-value so that $K_i > 1$ or if there is not even one $K$-value so that: $K_i < 1$, then the desired interval containing the root sought does not exist. In this case $\Psi$ is directly set to 0 if all $K_i < 1$ or $\Psi$ is set to 1 if all $K_i > 1$.

If there is at least one K-value so that $K_i > 1$ and one K-value so that $K_i < 1$ we obtain:

$$\Psi_{LB} = -\frac{1}{K_{iMax} - 1}$$

$$\Psi_{UB} = -\frac{1}{K_{iMin} - 1}$$

Then $\Psi$ can be determined by a Newton-Raphson iteration:

$$\Psi_{n+1} = \Psi_n - G_n / G'_n$$

One bound may be tightened (because G is monotonic):

$$\text{if } G_n > 0 \qquad \Psi_{LB} = \Psi_n$$
$$\text{if } G_n < 0 \qquad \Psi_{UB} = \Psi_n$$

The vapour fraction $\Psi_{n+1}$ is constrained so that:

$$\Psi_{LB} < \Psi_{n+1} < \Psi_{UB}$$

Convergence is assumed when:

$$\left| \Psi_{n+1} - \Psi_n \right| \leq \text{TOL} = \text{Max}(0.00001 , 0.00001 \left| \Psi_{n+1} \right| )$$

Then we set the outer loop variable:

$$\Psi_m = \Psi_n$$

If $\Psi_n < 0$ we set $\Psi_n = 0$ to get $y_i$ & $x_i$

If $\Psi_n > 1$ we set $\Psi_n = 1$ to get $y_i$ & $x_i$

($\Psi$ is physically meaningful when $0 \leq \Psi \leq 1$)

# Appendix H. Details of solution method (isenthalpic, isentropic, or constant energy flash)

This vapour-liquid equilibrium calculation is used when the specified set of parameters are $P\&H_T$ or $P\&s_T$ or $P\&E_T$ (where the subscript $T$ indicates the total quantity) and the temperature $T$ is unknown.

The main steps in the method are as follows:

1. Call FLTPVF to calculate the dew point temperature ($T_{DP}$), as described in Appendix B.

2. Calculate the dew point enthalpy $H_{v,DP}$, entropy $s_{v,DP}$, or energy $E_{v,DP}$.

3. If $H_T > H_{v,DP}$ (or the equivalent for entropy or energy) call FLTFND as described in Section H.2 to calculate $T$ of superheated vapour. Go to Step 8.

4. Call FLTPVF to calculate bubble point $T$ ($T_{BP}$), as described in Appendix B.

5. Calculate bubble point enthalpy $H_{v,BP}$, entropy $s_{v,BP}$, or energy $E_{v,BP}$.

6. If $H_T < H_{v,BP}$ (or the equivalent for entropy or energy) call FLTFND as described in H.2 to calculate $T$ of subcooled liquid. Go to Step 8.

7. If $H_{v,BP} < H_T < H_{v,DP}$ (or the equivalent for entropy or energy) call FLHSP as described in Section H.1 to calculate $T\&\Psi$ of the vapour-liquid mixture.

8. Calculate $h, s, p, M$ for each phase and total fluid.

The symbols used are described at the end of the appendix.

## H.1 Isenthalpic - Isentropic Flash (FLHSP)

The algorithm matches the specified molar enthalpy (h) or entropy (s) for a two-phase vapour liquid fluid at specified P. A bounded secant method is used to iterate on vapour fraction ($\psi$) to locate the root of:

$$G = h - h_{SPEC}$$

or

$$G = s - s_{SPEC}$$

or

$$G = E - E_{SPEC}$$

Subroutine FLTPVF is called for each trial value of $\Psi$ to determine T and phase compositions.

1. The base tolerance for the root of $G$ is:
$$TOL_o = 0.0004184 \times M \text{ J/gmole, for enthalpy}$$
$$= 0.000004184 \times M \text{ J/gmole/K, for entropy}$$

Bounds:
$$\Psi_{UL} = 1$$
$$\Psi_{LL} = 0$$

2. Given $\Psi o$ calculate $Go$

Convergence is assumed if $\left| Go \right| \langle TOL_0$ .

If Go < 0 Iterate $\Psi_{k+1} = \Psi_k + 0.05$ incrementally until $G_k > 0.0$, and then set:

$$\Psi_{LL} = \Psi_{k-1}$$

If Go > 0 Iterate $\Psi_{k+1} = \Psi_k - 0.05$ incrementally until $G_k < 0.0$, and then set:

$$\Psi_{UL} = \Psi_{k-1}$$

3. The root is now bracketed between:

$$\Psi_{LL} < \Psi < \Psi_1 \text{ or } \Psi_1 < \Psi < \Psi_{UL}$$

where $\Psi_1 = \Psi_k$ from 2.

Further iteration is by secant formula:

$$\Delta\Psi = \Psi_n - \Psi_{n-1}$$
$$\Delta G = G_n - G_{n-1}$$

If $\left|\Delta\Psi\right| < 0.00001 \text{ } and \text{ } \left|G_n\right| > TOL_o$ the algorithm has failed.

Otherwise the tolerance is set to: $TOLR = MAX \text{ } (TOL_o, \text{ } TOL_n)$

Where $TOL_n = 0.00002 \left|\Delta G / \Delta\Psi\right|$

If $|G_n| \leq TOLR$ and $|\Delta\Psi| < 0.0001$ convergence is assumed

Otherwise the iteration continues.

If $|\Delta G / \Delta\Psi| < 10^{-8}$ the algorithm has failed.

Otherwise the secant formula is applied:

$$\Psi_{n+1} = \Psi_n - G_n / \left(\Delta G / \Delta\Psi\right)$$

One of the bounds is adjusted:

$$\text{If } G_n < 0 \quad \Psi_{LL} = \Psi_n$$
$$\text{If } G_n > 0 \quad \Psi_{UL} = \Psi_n$$

$\Psi_{n+1}$ is then bounded:

$$\text{If } \Psi_{n+1} > \Psi_{UL} \quad \Psi_{n+1} = \left(\Psi_n + \Psi_{UL}\right)/2$$
$$\text{If } \Psi_{n+1} < \Psi_{LL} \quad \Psi_{n+1} = \left(\Psi_n + \Psi_{LL}\right)/2$$

and the iteration continues.

## H.2 Single Phase Isenthalpic - Isentropic flash (FLTFND)

The algorithm matches specified molar enthalpy (h) or entropy (s) for a single-phase vapour or liquid fluid at specified pressure (P). The secant method is used to find the root T of specification function G:

$$G = h - h_{SPEC}$$

Or

$$G = s - s_{SPEC}$$

Or

$$G = E - E_{SPEC}$$

1.      The base tolerance for the root of G is:

$$TOL_o = 0.0004184 \text{xM J/gmole, for enthalpy}$$
$$= 0.000004184 \text{xM J/gmole/K, for entropy}$$

2.      Given $T_0$ where:

$$T_o > T_{DP} + 5. \quad \text{If } \Psi = 1.0$$
$$T_o < T_{BP} - 5. \quad \text{If } \Psi = 0.0$$

Let:

$$T_1 = T_o - 5.$$
$$T_2 = T_o + 5.$$

4.   Iterate by secant method
5.

$$\Delta G = G_k - G_{k-1}$$
$$\Delta T = T_k - T_{k-1}$$
$$\text{If } |G_k| < TOL \text{ and } |\Delta T| < 0.05 \quad \text{convergence is assumed}$$
$$\text{If } |\Delta G| < 10^{-8} \text{ and } |\Delta T| < 0.001 \quad \text{algorithm failure is assumed}$$

The tolerance is reset:

$$TOL = Max\left(TOL_o, TOL_k\right)$$

Where

$$TOL_k = 0.002\left|\Delta G/\Delta T\right|$$
$$TOL_{k-1} = T_k - G_k/\left(\Delta G/\Delta T\right)$$
$$\text{If } T_{k+1} > T_{UL} \quad T_{k+1} = \left(T_k + T_{UL}\right)/2$$
$$T_{k+1} < T_{LL} \quad T_{k+1} = \left(T_k + T_{LL}\right)/2$$

and the iteration continues.

# Appendix I.  Emulating pseudo-component equilibrium in new property system

This Appendix discussed the method with which the new multi-component property system XPRP (MC) would be able to emulate the method of 'pseudo-component' equilibrium (PC) applied in the old property system PRP.

There are two fundamental principles that define the PC methodology:

1. Regardless of phase fractions, the compositions of all phases are identical

2. The determination of phase fraction is determined by reference to the mixture bubble point using ideal thermodynamic methods (i.e. vapour pressure)

In MC methods, when using ideal thermodynamics for both the vapour and liquid phases, the equilibrium compositions are defined by:

$$y_i P = x_i P_i^{sat} \qquad (216)$$

Therefore the bubble point pressure is defined by:

$$P_{bub} = \sum x_i P_i^{sat} \qquad (217)$$

These can be reformulated in terms of the familiar K value as:

$$y_i = K_i x_i \qquad (218)$$

Where

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P} \qquad (219)$$

Therefore, if we wanted an MC method that behaved like the PC method we require that

$$K_i = 1 \text{ (for all i)} \qquad (220)$$

This can only be achieved if, in calculating the K values, the vapour pressure that is used is the same for all components, i.e.

$$P_i^{sat} = P_*^{sat} \text{ (for all i)} \qquad (221)$$

If this were the case, then to match the bubble point pressure we require that:

$$P_{bub} = \sum x_i P_i^{sat} = \sum x_i P_*^{sat} = P_*^{sat} \qquad (222)$$

Such a method could be implemented in the new property system as a liquid phase fugacity option[36]. The calculation of vapour pressure would take the form:

$$P_*^{sat} = \sum x_i P_i^{sat} \qquad (223)$$

which would then be used as the vapour pressure for every component.

The fact that the K values are now identical for every component means that the flash algorithm behaves very much as if the mixture is a pure component:

1. The vapour and liquid compositions will always be identical.

---

[36] ERROR.  This has been done, but I think at the moment it doesn't work.  To test in more detail.

2. In a fixed vapour fraction flash, the calculated temperature or pressure will correspond to the ideal bubble point of the mixture.

3. In a fixed temperature and pressure flash, the phase fraction will always be returned as either 0 or 1 depending on whether the K value is less than or greater than 1.

This seems to satisfy the requirements of the current PC approach, but is implemented solely by configuration of the fugacity method on the stream type. Furthermore, calculated properties can be retrieved in a consistent manner irrespective of the PC/MC setting.

All the usual flash types should work correctly. For example, for an isenthalpic flash, while iterating for a solution on vapour fraction, the vapour and liquid compositions will be the same. However, the vapour enthalpy will still be calculated using the vapour enthalpy method and the liquid enthalpy will still be calculated using the liquid enthalpy method. So if these are the same as in PC, the same answers will be obtained between PC and MC.

# Appendix J. Implementation of property calculation in new property system (XPRP)

This appendix contacts logic corresponding to code implementation into new property system XPRP, as far as is different as described in the main body of this report.

## *J.1* Cubic equations of state

Redlich-Kwong Equation

This is one of the simplest cubic equations of state, and because of its limitations in some areas was modified by Soave as shown below. The original Redlich-Kwong equation for component i is:

$$P = \frac{RT}{v - b_i} - \frac{a_i}{v(v - b_i)\sqrt{T}} \qquad (224)$$

Where

$$a_i = 0.4278 \frac{R^2 T_{ci}^{2.5}}{P_{ci}} \qquad (225)$$

and

$$b_i = 0.0867 \frac{RT_{ci}}{P_{ci}} \qquad (226)$$

For mixtures, equivalents to *a* and *b* must be defined:

$$\overline{a} = \frac{\sum y_i \sqrt{a_i}}{R} \qquad (227)$$

$$\overline{A} = \frac{\overline{a}}{\sqrt{T^{2.5}}} \qquad (228)$$

$$\overline{B} = \frac{\sum y_i b_i}{RT} \qquad (229)$$

and the compressibility can then be expressed as a cubic:

$$Z^3 - Z^2 + Z\left[\overline{A}^2 P - \overline{B}P\left(1 + \overline{B}P\right)\right] - \left(\overline{A}^2 P\right)\left(\overline{B}P\right) = 0 \qquad (230)$$

Note that this is an identical equation to that for SRK below, but the definitions of the A and B terms differ.

Also, in this implementation, binary interaction parameters are not used.

Soave-Redlich-Kwong Equation[37]

$$P = \frac{RT}{v - \overline{b}} - \frac{\overline{a}\alpha}{v(v + \overline{b})} \qquad (231)$$

$$\overline{b} = \sum_i z_i \frac{b_i}{R} = \sum_i z_i 0.08664 \frac{T_{c,i}}{P_{c,i}} \qquad (232)$$

---

[37] ERROR. The constants currently used in the following equations are not as written, but are those used for the old property system. This is to minimise differences in regression testing between the two systems, and should be reverted once we are satisfied with the new system. VI6407.

$$\overline{a\alpha} = R^2 \sum_i \sum_j z_i z_j c_{ij} \sqrt{a_i'} \sqrt{\alpha_i} \sqrt{a_j'} \sqrt{\alpha_j}$$

( 233 )

$$a_i' = \frac{a_i}{R} = 0.42747 \frac{T_{c,i}^2}{P_{c,i}}$$

( 234 )

$$\alpha_i = \left[ 1 + f_{\omega,i} \left( 1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2$$

( 235 )

$$f_{\omega,i} = 0.48508 + 1.55171 \omega_i + 0.15613 \omega_i^2$$

( 236 )

$$c_{ij} = c_{ji} = (1 - k_{ij})$$

( 237 )

In the equations above:

$z_i$       is the mole fraction of component $i$ in the phase under consideration
$T_{c,i}$     is the critical temperature of component $i$
$P_{c,i}$     is the critical pressure of component $i$
$\omega$       is the acentric factor for the material, a constant given by[38]:

$$\omega = -\log_{10} \left[ \frac{P_{sat}(T = 0.7 T_c)}{P_c} \right] - 1$$

( 238 )

where $P_{sat}(T)$ is the saturation pressure at the specified temperature (i.e. at $0.7 T_c$).
$c_{ij}$, $c_{ji}$    are symmetric binary interaction parameters
$k_{ij}$      is the binary interaction constant
The equation can be expressed in terms of the compressibility $Z$ as follows:

$$Z^3 - Z^2 + Z\left[ \overline{A}^2 P - \overline{B}P\left( 1 + \overline{B}P \right) \right] - \left( \overline{A}^2 P \right)\left( \overline{B}P \right) = 0$$

( 239 )

$$Z = \frac{Pv}{RT}$$

( 240 )

$$\overline{A}^2 = \frac{\overline{a\alpha}}{T^2}$$

( 241 )

$$\overline{B} = \frac{\overline{b}}{T}$$

( 242 )

Peng-Robinson Equation

---

[38] Although acentric factor can be calculated, for most materials it is provided in the DIPPR database. It is only calculated in the new system if no value is found.

$$P = \frac{RT}{v - \bar{b}} - \frac{\overline{a\alpha}}{v(v + \bar{b}) + \bar{b}(v - \bar{b})}$$

(243)

$$\bar{b} = \sum_i z_i \frac{b_i}{R} = \sum_i z_i \, 0.07780 \frac{T_{c,i}}{P_{c,i}}$$

(244)

$$a_i' = \frac{a_i}{R} = 0.45724 \frac{T_{c,i}^2}{P_{c,i}}$$

(245)

$$\overline{a\alpha} = R^2 \sum_i \sum_j z_i z_j c_{ij} \sqrt{a_i'} \sqrt{\alpha_i} \sqrt{a_j'} \sqrt{\alpha_j}$$

(246)

$$\alpha_i = \left[ 1 + f_{\omega,i} \left( 1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2$$

(247)

$$f_{\omega,i} = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

(248)

$$c_{ij} = c_{ji} = (1 - k_{ij})$$

(249)

The three constants used in Equation ( 248 ) were determined to fit pure component vapour pressures by Peng and Robinson.

The equation can be expressed in terms of the compressibility $Z$ as follows:

$$Z^3 - Z^2\left[1 - \bar{B}P\right] + Z\left[\bar{A}^2 P - \bar{B}P\left(2 + 3\bar{B}P\right)\right] - \left(\bar{A}^2 P - \bar{B}P\left(1 + \bar{B}P\right)\right)\left(\bar{B}P\right) = 0$$

(250)

where all terms are as for Soave-Redlich-Kwong.

## J.2 Enthalpy

Redlich-Kwong Equation

$$\frac{\Delta H}{RT} = -1.5 \frac{\bar{A}^2}{\bar{B}} \ln\left(1 + \frac{\bar{B}P}{Z}\right) - (1 - Z)$$

(251)

Note that the A and B terms are as in the Redlich-Kwong discussion above, not as used by Soave-Redlich-Kwong and Peng-Robinson

Soave-Redlich-Kwong Equation

$$\left[\frac{\Delta H}{RT}\right] = \frac{\overline{A}^2}{\overline{B}}\ln\left(1+\frac{\overline{B}P}{Z}\right)\left\{2\frac{SUM}{a\alpha}-1\right\}-(1-Z)$$

( 252 )

$$SUM = \sum_i z_i(a\alpha)_i \frac{T}{\alpha_i^{1/2}}\frac{\partial \alpha_i^{1/2}}{\partial T}$$

( 253 )

Peng-Robinson Equation

$$\left[\frac{\Delta H}{RT}\right] = \frac{\overline{A}^2}{2\sqrt{2}\overline{B}}\left[2\frac{SUM}{a\alpha}-1\right]\ln\left(\frac{Z+(1+\sqrt{2})\overline{B}P}{Z+(1-\sqrt{2})\overline{B}P}\right)-(1-Z)$$

( 254 )

## *J.3* Entropy

Redlich-Kwong Equation

$$\frac{\Delta S}{R} = -\frac{\overline{A}^2}{\overline{B}}\ln\left(1+\frac{\overline{B}P}{Z}\right)+\ln\left(\frac{Z-\overline{B}P}{P}\right)+\ln(P)$$

( 255 )

Soave-Redlich-Kwong Equation

$$\left[\frac{\Delta s}{R}\right] = 2\frac{\overline{A}^2}{\overline{B}}\frac{SUM}{a\alpha}\ln\left(1+\frac{\overline{B}P}{Z}\right)+\ln\left(\frac{Z-\overline{B}P}{P}\right)+\ln(P)$$

( 256 )

Peng-Robinson Equation

$$\left[\frac{\Delta s}{R}\right] = \frac{\overline{A}^2}{2\sqrt{2}\overline{B}}\frac{2SUM}{a\alpha}\ln\left(\frac{Z+(1+\sqrt{2})\overline{B}P}{Z+(1-\sqrt{2})\overline{B}P}\right)+\ln\left(\frac{Z-\overline{B}P}{P}\right)+\ln(P)$$

( 257 )

## *J.4* Fugacity coefficient

Redlich-Kwong Equation

$$\ln\hat{\varphi}_i = -\ln(Z-\overline{B}P)-\left[\frac{2}{\overline{a}}\frac{\overline{A}^2}{\overline{B}}\ln\left(1+\frac{\overline{B}P}{Z}\right)\right]\sqrt{a_i'}-\left[(1-Z)-\frac{\overline{A}^2}{\overline{B}}\ln\left(1+\frac{\overline{B}P}{Z}\right)\right]\frac{b_i'}{\overline{b}}$$

( 258 )

$$a_i' = \frac{a_i}{R^2}$$

( 259 )

$$b_i' = \frac{b_i}{R}$$

( 260 )

$$\overline{b} = \overline{B}T$$

( 261 )

Soave-Redlich-Kwong Equation

$$\ln \hat{\phi}_i = -\ln\left(Z - \overline{B}P\right) - \left[\frac{2}{\overline{a\alpha}}\frac{\overline{A}^2}{\overline{B}}\ln\left(1 + \frac{\overline{B}P}{Z}\right)\right](a\alpha)_i$$

$$-\left[(1 - Z) - \frac{\overline{A}^2}{\overline{B}}\ln\left(1 + \frac{\overline{B}P}{Z}\right)\right]\frac{1}{\overline{b}}\ b_i'$$

( 262 )

$$b_i' = 0.08664\,\frac{T_{c,i}}{P_{c,i}}$$

( 263 )

Peng-Robinson Equation

$$\ln \hat{\phi}_i = -\ln\left(Z - \overline{B}P\right) - \left[\frac{Z\overline{A}^2}{2\sqrt{2}\ \overline{B}\ \overline{a\alpha}}\ln\left(\frac{Z + \left(1 + \sqrt{2}\right)\overline{B}P}{Z + \left(1 - \sqrt{2}\right)\overline{B}P}\right)\right](a\alpha)_i$$

$$+\left\{\left[\frac{\overline{A}^2}{2\sqrt{2}\ \overline{B}}\ln\left(\frac{Z + \left(1 + \sqrt{2}\right)\overline{B}P}{Z + \left(1 - \sqrt{2}\right)\overline{B}P}\right) - (1 - Z)\right]\frac{1}{\overline{b}}\right\}b_i'$$

( 264 )

$$b_i' = 0.07780\,\frac{T_{c,i}}{P_{c,i}}$$

( 265 )

## J.5 Isothermal compressibility

Soave-Redlich-Kwong Equation

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{ZRT}{P^2}\left[\frac{P\left(\frac{\partial d}{\partial P}\right)_T - ZP\left(\frac{\partial c}{\partial P}\right)_T}{Z\left(3Z^2 - 2Z + c\right)} - 1\right]$$

( 266 )

$$c = \overline{A}^2 P - \overline{B}P\left(1 + \overline{B}P\right) \quad P\left(\frac{\partial c}{\partial P}\right)_T = c - \overline{B}P^2$$

( 267 )

$$d = \left(\overline{A}^2 P\right)\left(\overline{B}P\right) \quad P\left(\frac{\partial d}{\partial P}\right)_T = 2d$$

( 268 )

Peng-Robinson Equation

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{ZRT}{P^2}\left[\frac{P\left(\frac{\partial d}{\partial P}\right)_T - ZP\left(\frac{\partial c}{\partial P}\right)_T + Z^2 P\left(\frac{\partial b}{\partial P}\right)_T}{Z\left(3Z^2 - 2bZ + c\right)} - 1\right]$$

( 269 )

$$b = \left(1 - \overline{B}P\right) \quad P\left(\frac{\partial b}{\partial P}\right)_T = -\overline{B}P$$

( 270 )

$$c = \overline{A}^2 P - \overline{B}P\left(2 + 3\overline{B}P\right) \quad P\left(\frac{\partial c}{\partial P}\right)_T = c - 3\overline{B}P^2$$

( 271 )

$$d = \overline{B}P\left[\overline{A}^2 P - \overline{B}P\left(1 + \overline{B}P\right)\right] \quad P\left(\frac{\partial d}{\partial P}\right)_T = 2d - \overline{B}P^3$$

( 272 )

## J.6 Coefficient of Thermal Expansion

Soave-Redlich-Kwong Equation

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{ZR}{P}\left[\frac{T\left(\frac{\partial d}{\partial T}\right)_P - ZT\left(\frac{\partial c}{\partial T}\right)_P}{Z\left(3Z^2 - 2Z + c\right)} + 1\right]$$

( 273 )

$$c = \overline{A}^2 P - \overline{B}P\left(1 + \overline{B}P\right) \quad T\left(\frac{\partial c}{\partial T}\right)_P = 2\frac{P}{T^2}SUM - 2\overline{A}^2 P + \overline{B}P\left(1 + 2\overline{B}P\right)$$

( 274 )

$$d = \left(\overline{A}^2 P\right)\left(\overline{B}P\right) \quad T\left(\frac{\partial d}{\partial T}\right)_P = 2\overline{B}P\frac{P}{T^2}SUM - 3\left(\overline{A}^2 P\right)\left(\overline{B}P\right)$$

( 275 )

Peng-Robinson Equation

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{ZR}{P}\left[\frac{T\left(\frac{\partial d}{\partial T}\right)_P - ZT\left(\frac{\partial c}{\partial T}\right)_P + Z^2 T\left(\frac{\partial b}{\partial T}\right)_P}{Z\left(3Z^2 - 2bZ + c\right)} + 1\right]$$

( 276 )

$$b = \left(1 - \overline{B}P\right) \quad T\left(\frac{\partial b}{\partial T}\right)_P = \overline{B}P$$

( 277 )

$$c = \overline{A}^2 P - \overline{B}P\left(2 + 3\overline{B}P\right) \quad T\left(\frac{\partial c}{\partial T}\right)_P = 2\frac{P}{T^2}SUM - 2\overline{A}^2 P + \overline{B}P\left(2 + 3BP\right)$$

( 278 )

$$d = \overline{B}P\left[\overline{A}^2 P - \overline{B}P\left(1 + \overline{B}P\right)\right]$$
$$T\left(\frac{\partial d}{dT}\right)_P = \overline{B}P\left[2\frac{P}{T^2}SUM - 3\overline{A}^2 P + \overline{B}P\left(2 + 3\overline{B}P\right)\right]$$

( 279 )

## J.7 Specific heat capacities

**Soave-Redlich-Kwong Equation**

$$\left[\frac{\Delta C_v(T,P)}{R}\right] = \frac{2}{a\alpha}\frac{\overline{A}^2}{\overline{B}}\ln\left(1+\frac{\overline{B}P}{Z}\right)[SUM2+SUM3]$$

( 280 )

$$SUM2 = \sum_i z_i(a\alpha)_i\left[\frac{T^2}{\alpha_i^{1/2}}\frac{\partial^2\alpha_i^{1/2}}{\partial T^2}\right]$$

( 281 )

$$SUM3 = \sum_i z_i\left[\frac{T}{\alpha_i^{1/2}}\frac{\partial\alpha_i^{1/2}}{\partial T}\right]\sum_j z_j\left[\frac{T}{\alpha_j^{1/2}}\frac{\partial\alpha_j^{1/2}}{\partial T}\right]a_{ij}$$

( 282 )

**Peng-Robinson Equation**

$$\left[\frac{\Delta C_v(T,P)}{R}\right] = \frac{2}{a\alpha}\frac{1}{2\sqrt{2}}\frac{\overline{A}^2}{\overline{B}}\ln\left(\frac{Z+(1+\sqrt{2})\overline{B}P}{Z+(1-\sqrt{2})\overline{B}P}\right)[SUM2+SUM3]$$

( 283 )

# Appendix K.  Implementation of property calculation in old property system (PRP)

This appendix contacts logic corresponding to code implementation into old property system PRP, as far as it is different (including notation) as described in the main body of this report.

<u>Cubic equation of state</u> (same as in body of report but using different notation)

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2}$$

(284)

where $a$, $b$, $u$ and $w$ are constants defined below for each of the equations.

This equation can be re-stated as a cubic equation in Z (the compressibility):

$$Z^3 - \left(1 + B^* - uB^*\right)Z^2 + \left(A^* + wB^{*2} - uB^* - uB^{*2}\right)Z - A^*B^* - wB^{*2} - wB^{*3} = 0$$

(285)

where:

$$A^* = \frac{aP}{R^2T^2} \quad \text{and} \quad B^* = \frac{bP}{RT}$$

(286)

Each of the three cubic equations of state uses different values for the four constants (a, b, u, w), as shown below.

| Equation of State | $u$ | $w$ | $b$ | $a$ |
|---|---|---|---|---|
| Redlich-Kwong | 1 | 0 | $\dfrac{0.08664RT_c}{P_c}$ | $\dfrac{0.42748R^2T_C^{2.5}}{P_cT^{0.5}}$ |
| Soave-Redlich-Kwong | 1 | 0 | $\dfrac{0.08664RT_c}{P_c}$ | $\dfrac{0.42748R^2T_C^2}{P_cT^{0.5}}\left[1 + f_\omega\left(1 - T_r^{0.5}\right)\right]^2$ where: $f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$ |
| Peng-Robinson | 2 | -1 | $\dfrac{0.07780RT_c}{P_c}$ | $\dfrac{0.45724R^2T_C^2}{P_cT^{0.5}}\left[1 + f_\omega\left(1 - T_r^{0.5}\right)\right]^2$ where: $f_\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$ |

<u>Helmholtz energy and entropy</u>

$$(A - A_{ref}) = -RT\ln\left(\frac{V-b}{V}\right) + \frac{a}{b\sqrt{u^2-4w}}\ln\left(\frac{2V+b(u-\sqrt{u^2-4w})}{2V+b(u+\sqrt{u^2-4w})}\right)$$

$$- RT\ln\left(\frac{V}{V_{ref}}\right)$$

(287)

$$(S - S_{ref}) = R\ln\left(\frac{V-b}{V}\right) + \frac{1}{b\sqrt{u^2-4w}}\ln\left(\frac{2V+b(u-\sqrt{u^2-4w})}{2V+b(u+\sqrt{u^2-4w})}\right)\left(\frac{da}{dT}\right)$$

$$+ R\ln\left(\frac{V}{V_{ref}}\right)$$

(288)

# NOMENCLATURE AND NOTATION

*Definitions and notation*:

| | |
|---|---|
| $a$ | parameter of cubic equation of state, Nm$^4$ |
| $A^*$ | transformed $a\alpha$ parameter of a cubic equation of state, $A^* = a\alpha P / (R^2T^2)$ , - |
| $b$ | parameter of cubic equation of state, m$^3$ |
| B | 2$^{nd}$ Virial Coefficient in virial equation, m$^3$ |
| $B^*$ | transformed b-parameter of cubic equation, $B = bP / (R^2T^2)$, - |
| D | Intermediate parameter defined by $D_i = \Psi K_i + 1 - \Psi$ |
| $C_p$ | ideal gas heat capacity, J/(kmol K) |
| $f_\omega$ | Function of the acentric factor, - |
| F | Total feed rate, kmol/s |
| G | Gibbs free energy or deviation function, specification function |
| $H_{ig}(T)$ | ideal gas enthalpy at temperature T, J/kmol/K |
| $H_{vap}$ | heat of vaporisation, J/kmol |
| $H(T,P)$ | enthalpy at temperature T and pressure P, J/kg |
| K | Phase-equilibrium K-value |
| L | Liquid rate leaving, kmol/s |
| MW | Relative molecular mass, kg/kmol |
| N or NC | Number of components |
| $p$ | Pressure (partial or component), Pa |
| $P$ | Pressure (total), Pa |
| $P_c$ | Critical pressure, Pa |
| $P_{sat}(T)$ | Saturation pressure at temperature $T$, Pa |
| R | Universal gas constant= 8314.4 J/(kmol K) |
| $S(T,P)$ | entropy (at temperature $T$ and pressure $P)$ |
| T | Temperature, K |
| $T_c$ | Critical temperature, K |
| $T_r$ | Reduced temperature ($T/T_c$), - |
| $T_{sat}(P)$ | saturation temperature at pressure $P$, K |
| TOL | Iteration variable tolerance |
| U | internal energy |
| $u$ | $=1/T$ |
| V | molar volume, m$^3$/kmol |
| V | Vapour rate leaving, kmol/s |
| $x_i$ | Liquid mole fraction of component $i$ |
| $x_W$ | Liquid mole fraction of water |
| **x** | Vector of liquid mole fractions |
| $y_i$ | Vapour mole fraction of component $i$ |
| $y_W$ | Vapour mole fraction of water |
| **y** | Vector of vapour mole fractions |
| $z_i$ | Feed mole fraction of component $i$ |
| **z** | Vector of feed stream mole fractions |
| Z | Compressibility of the material $Z = PV/(RT)$ |

## Greek Symbols

| | |
|---|---|
| $\alpha$ | Temperature dependent parameter of cubic equation of state (-) |
| $\Delta H$ | Molar enthalpy departure function |
| $\Delta S$ | Molar entropy departure function |
| $\hat{\phi}$ | Fugacity coefficient of a component in a mixture |
| $\Psi$ | V/F i.e. the vapour fraction |
| $\omega$ | Acentric factor of a material |
| {} | Vector quantity. The dimension is typically the number of components NC |

## Subscripts

| | |
|---|---|
| BP | Bubble point |
| C | Critical property |
| DP | Dew point |

| | |
|---|---|
| HC | Hydrocarbon component (any component except separated water) |
| i | Ith component |
| ig | Ideal Gas |
| L | Liquid phase |
| LB | Lower Bound |
| m | Outer loop iteration counter |
| n | Inner loop iteration counter |
| o | Initial value |
| ref | reference state for departure functions (ideal gas at same composition and same P,T) |
| REF | reference state for zero enthalpy/entropy; $T_{REF}$ = 298.15K, $P_{ref}$ = 1Pa |
| sat | Saturated condition |
| SPEC | Specified parameter |
| T | At temperature T |
| UB | Upper Bound |
| v | Vapour phase |
| W | Water |

*Superscripts*

*        Composition dependent value held fixed

## About DNV

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