Thermotools memo

Flexible thermodynamic workbench for CCS thermodynamics

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1 Introduction

In the project CO_2 Dynamics, the overall aim is to provide knowledge about safe and efficient design and operation of CO_2-pipeline transport and injection systems. To achieve this, knowledge about the thermo-physical properties of CO_2-mixtures is needed. Thermo-physical properties can be densities, viscosities, heat capacities and much more. Since these are necessary input to all higher level modeling, accurate, robust and fast theoretical models are prerequisites for reliable

process and scenario evaluations. CO_2-Dynamics started already in 2009. In 2009 and 2010, in-house thermodynamic routines were tested and used to do regression of interaction parameters for cubic equations of state capable of handling CO_2 mixtures. This was documented in the memo DA1001. In 2011, other equations of state such as Lee-Kesler and the SPUNG approach were tested for CO_2-mixtures and presented in a paper (DA1103). In other projects, the risk of hydrate-formation has been studied [2]. To avoid hydrate formation and freeze-out of water in pipelines where CO_2 is transported is vital for safe operation. A lesson learned in all these projects is that there are many scientific challenges associated with thermo-physical phenomena in CCS-operations. To be able to handle these, a flexible yet powerful computational framework is necessary. Flexibility is needed because new parameters, models and experimental data will be available for CO_2-systems in the years to come. It should be simple and fast to implemented and test these in a feasible computational framework. In addition, regression of interaction coefficients and other parameters for CO_2-systems requires the computational framework to be fast, since a multi-parameter-regression requires a large amount of function evaluations. Fortran 95 has been chosen as the computational basis for this flexible workbench for CO_2-thermodynamics, since it is one of the fastest computational languages available. This memo describes the initial development of the computational framework, and it also shows how the general three-parameter cubic equation of state can be implemented in the framework. Three-parameter cubic equations of state have properties which make them more suitable for use in CCS-systems than standard cubic EoS, namely that they can better handle polar components. In addition, analytical derivatives for the Huron-Vidal mixing rule has been derived, which enables a consistent implementation in the framework. The new computational framework for thermo-physical properties will be described in Sec. 2. How the general cubic EoS and non standard mixing rules can be implemented will be explained in Sec. 3, before concluding remarks are presented in Sec. 4.

2   Flexible workbench for thermo-physical properties

There are several requirements for a flexible workbench capable of handling the challenges arising in CCS-thermodynamics should be able to tackle:

1. The accuracy and robustness of already existing equations of state and models should easily be tested through fast and consistent implementations.

2. New models and equations of state for CO_2 rich mixtures should easily be implemented for further assessment.

3. Formation of solids such as ice or dry-ice (solid CO_2) at low temperatures/pressures should be taken into account.

4. The existence of several liquid phases in addition to a vapour phase is important. Examples are given for relevant CO_2 mixtures in the work by Austegard et al. [1].

5. New parameters for additional calculations, such as in hydrate-formation should easily be added to the model parameter library.

6. The workbench should be modular, easily maintained and updated.

7. Calculations should be fast enough such that they can be made available for other programs, such as fluid-dynamic codes, or process simulators. Regression of parameters for complex equations of state and linking with fluid-dynamic code and process simulations also require that the workbench is computationally fast.

8. Automatic routines for consistency checks will reduce the risk for errors in programming or development of inconsistent thermo-physical models.

9. Plotting of phase-envelopes and other data should be available.

Motivated by the bullet points above, the development of a flexible thermodynamic workbench has been initiated. The thermodynamic workbench has been called "ThermoPack", which the workbench will be referred to in the remaining part of this memo. Since ThermoPack needs to be computationally fast and modular, the computational language chosen is Fortran 95. The program "Mercurial" has been used for version control since several researches have been working simultaneously in the development of ThermoPack. Fig 1 illustrates the structure of ThermoPack in which a layer-based model is used. Starting from the outer layer, the different layers can be described as follows:

Data base layer This is the layer at which component dependent parameters are stored for many components. This data can be critical temperatures, pressures or data for vapour-pressure or heat capacity models. As more components and parameters is added this layer will grow.

Internal data storage structure Since the data base layer is large, it is more practical to work with a more compact structure for the components and the models chosen, since only a subset of the data base layer is needed for most practical applications.

Initialization and selection structure This layer determines how the active components and models are chosen.

Model specific routines Once parameters for the chosen components and model parameters are available in the active structure, this layer consists of the model equations for specific models. One part of this layer can be the state functions for the cubic equations of state, another part could be the state functions for the Lee-Kesler equation of state.

Data base layer – read ascii input files and
generate internal data base (module)
Query routines

Internal data storage structure
(active components and methods)

Based on the active components
and the active database, this layer
belongs to the specific thermo-
physical model.

The driver routines calculates
general properties on the basis of
the specific model routines.

The core-routines is the inner layer,
general for their respective models.
The routines which are most
frequently called by the average user.

Init and selection

Model specific routines
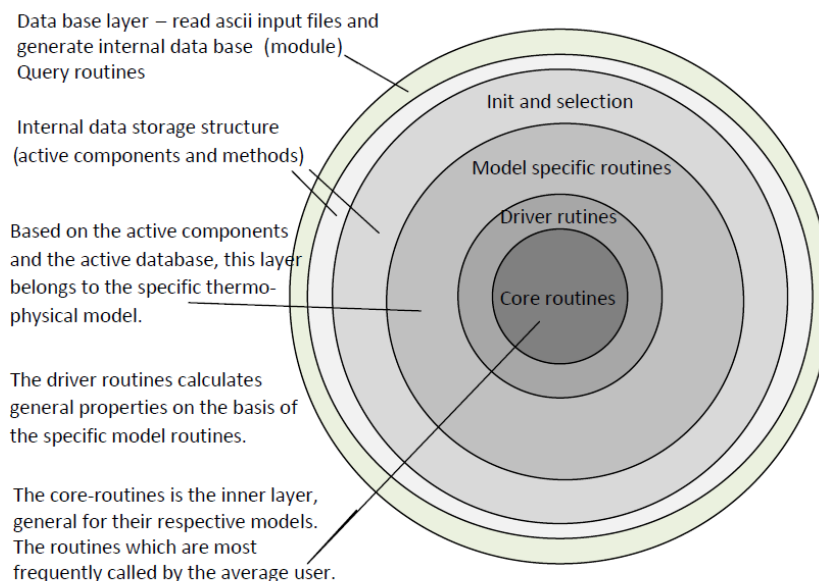
Driver rutines

Core routines

Figure 1: Description of routine layers

Driver routines These routines link the model specific routines to more general routines readily called from the core-routines. Here, operations such as automatic numerical derivation of all models in the model specific routines will be included.

Core routines The core routines are routines which only needs input from thermo-physical models. Examples are fugacity coefficients used in flash-routines, stability-routines and compressibility factor solver. These routines are those which most frequently are called from the user functions, but not necessary directly from a user level.

Add-on and utility routines These are the outermost routines and could be maintenance routines for the, regression of model parameters like binary interaction coefficients. Dedicated routines for solid formation detection, hydrate formation detection, plotting of various thermodynamic diagrams and so on.

The layers: **Data base layer, Internal data storage structure, initialization and selection structure and Driver routines** will be treated in more detail in the next sections. Model specific routines for the general cubic equation of state will be treated in the next sections. The following core routines will be treated in more detail in the memo DA1202: flash calculations at specified temperature and pressure (TP-flash), specified enthalpy and pressure (HP-flash), specified entropy and pressure (SP-flash), specified internal energy and volume (UV-flash) and the multiphase TP-flash.

2.1 Input format of parameters and data

In a thermodynamic package, each chemical component have their corresponding data such as critical temperatures, pressures, constants for ideal gas heat capacities and much more. The first layers in Fig. 1 is exemplified for equations of state in Fig. 2. Here it is illustrated how parameters for the components, and also parameters for the chosen equation of state (constants, mixing rules and interaction parameters) are read from the database and compiled into a more condense active structure. To make ThermoPack as flexible as possible, it has been decided to separate the mixing
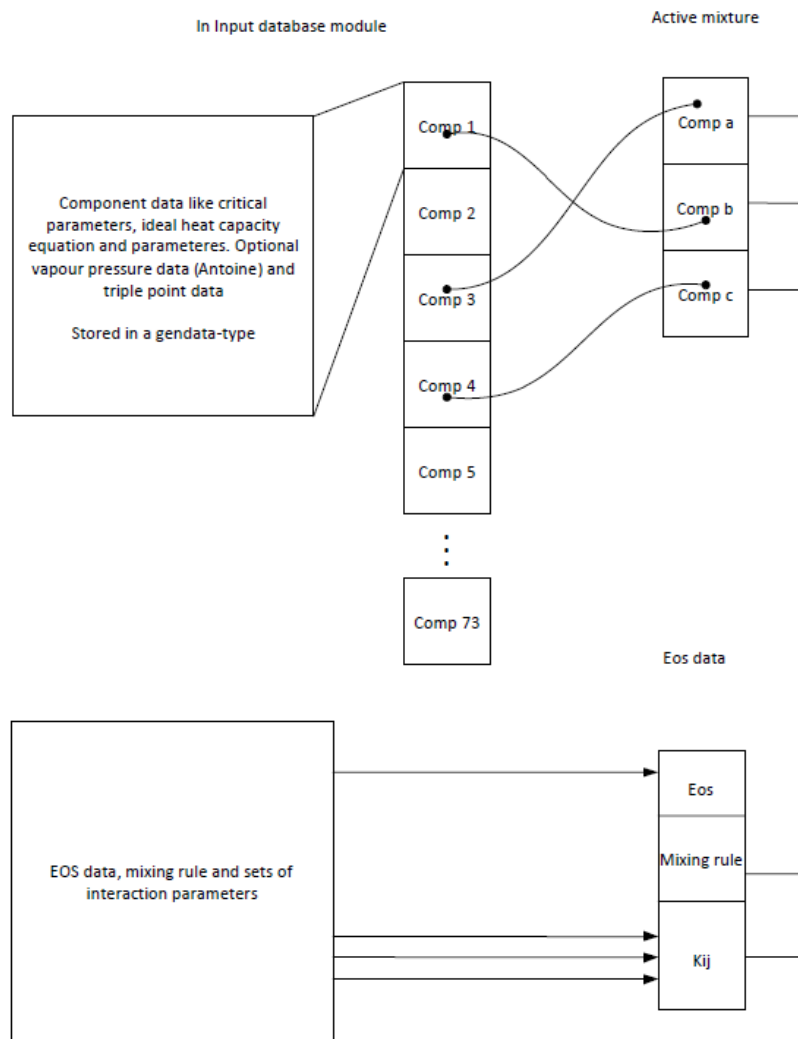
Figure 2: Description of equation of state structure

rule calculations from the equation of state calculations, such that each equation of state may be coupled to the available mixing rules (standard, Huron-Vidal, temperature dependent, ++). To achieve a simple and transparent program, a keyword-based data library has been chosen. An example is shown below:

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```
COMP CO2
      ID = CO2
      FORMULA = CO2
      NAME = CARBONDIOXIDE_(R744)
      MW =   44.01
      TCR =   304.2
      PCR =   7376500.
      ZCR =   0.274
      ACF =   0.225
      TB =    194.7
      PSATCODE =  1
      NPSAT =  3
      ANT =   22.5898  3103.39 -0.16
      TANTMIN =   154.
      TANTMAX =   204.
      NCPTYPE =  1
      CPTYPE =  7
      NCP = 5
      CP =   0.293700E+05  0.345400E+05  0.142800E+04  0.264000E+05  0.588000E+03
      TMINCP =   50.
      TMAXCP =   5000.
 END
```

Here, the currently available component data for CO_2 is shown. The keywords mean:

MW: mole-weight [kg/kmole]

TCR: Critical temperature [K]

PCR: Critical pressure [Pa]

ZCR: Critical compressibility factor [-]

ACF: Acentric factor [-]

TB: Boiling point [K]

PSATCODE: A flag for which model which should be chosen to calculate the pure component vapour pressure

NPSAT: Number of available models for pure component vapour-pressure calculations

ANT: Antoine vapour-pressure equation coefficients

TANTMIN: Minimum temperature for Antoine equation [K]

TANTMAX: Maximum temperature for Antoine equation [K]

NCPTYPE: Number of available ideal gas heat capacity model

CPTYPE: Flag which refers to the ideal gas model

NCP: Number of constants in ideal gas heat capacity model

CP: Parameters in ideal gas heat capacity model

TMINCP: Minimum temperature for ideal gas heat capacity model

TMAXCP: Maximum temperature for the ideal gas heat capacity model.

New parameters can easily be included into the structure with new keywords, which makes the structure easily expanded.

2.2 Driver routines for equations of state

A large number of thermodynamic state functions, derivatives and useful relations can be obtained from all equations of state. Many of these, are however given by the Maxwell relations, or general relations in thermodynamics and are not specific for each equation of state. We would thus like to implement a minimum of functions, hereby referred to as the necessary functions, and then let other thermodynamic relations be calculated from these. In ThermoPack, all state functions use temperature, pressure and composition as input variables, even if these are not the canonical variables [4]. Many choices can be made for which functions that are chosen as necessary, but for ThermoPack, the following functions have to be supplied for each new equation of state to be fully defined and used in most common applications:

- The compressibility factor, Z

- The enthalpy, H

- The entropy, S

- The fugacity coefficient, ϕ

With these functions at hand, the other state functions may be calculated from thermodynamic relations. Phase-equilibrium calculations at specified temperature and pressure are available by supplying the fugacity coefficients and compressibility factors. If the goal is to test an equation of state, and use it in most engineering applications, numerical derivatives of the necessary functions may be sufficiently accurate. If the thermodynamic code is connected to fluid-dynamic calculations, or other applications which require high accuracy for robust solution, the necessary functions must be supplied with analytical derivatives. How this is taken care of by the driver routines is illustrated in Fig. 3.

In the functions called from the core-routines (i.e: flash-calculations, compressibility factor solver), or the utility module (contains useful variables and relations), the flag=1 refers to analytic derivatives, and flag=2 refers to an automatic numerical derivation of the necessary functions. The automatic numerical derivation methodology is expected to be useful in the development of new CCS-thermodynamics because it means that new EoS may be tested more efficiently.

3 The general cubic equation of state

Cubic Equations of State (EoS) are equations which define the pressure in a thermodynamic system is a third-degree polynomial of the molar volume. Cubic equations of state are probably the most used EoS in engineering calculations, since they are simple, fast and still manage to give reasonable predictions of densities, heat capacities and vapour-liquid equilibrium properties of mixtures. In our computational framework, we would like to have a flexible implementation which allows a straightforward implementation of new EoS both to evaluate them for CCS-applications, and to equip them with suitable interaction parameters. Table 1 shows six EoS which all belong to the cubic EoS family, but have different properties and complexity:

The first four EoS; by Van der Waals, Redlich Kwong, Soave Redlich Kwong and Peng Robinson are two-constant equations, meaning that the EoS uses only two parameters (a and b). The three
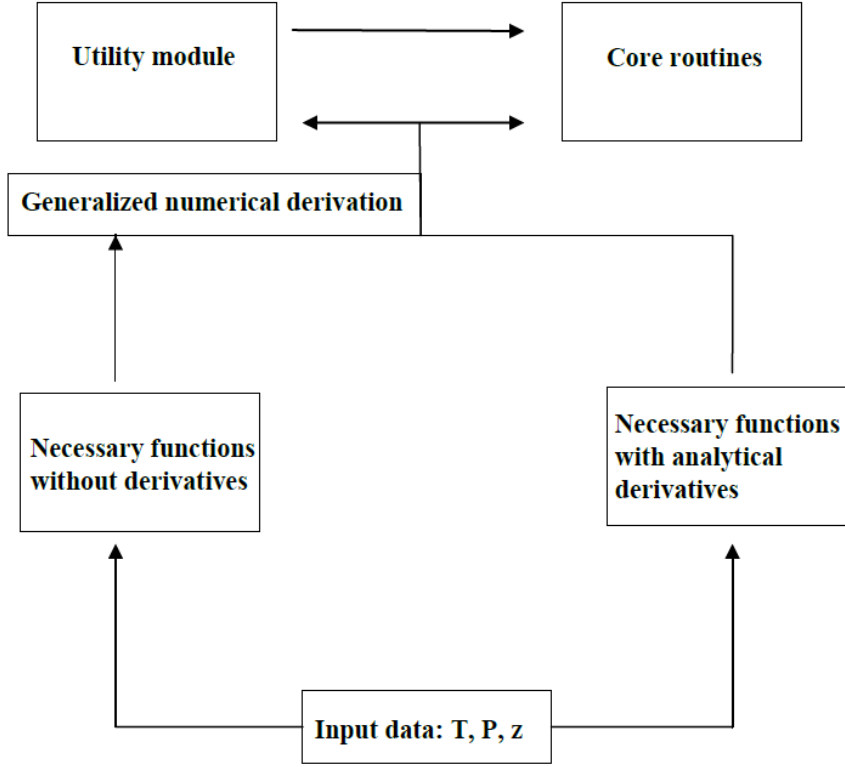
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Figure 3: Description of the concept behind the driver routines exemplified for EoS

next; by Schmidt-Wensel, Patel Teja and Yu-Lu are three parameter EoS, where the parameter "c" has been introduced. The EoS by Trebble-Bishnoi is a four-parameter EoS with the additional parameter "d". They can all be written in the following general expression for cubic EoS:

$$P = \frac{RT}{v - b} - \frac{a\alpha(T)}{(v - b(T)m_1)(v - b(T)m_2)} \tag{1}$$

In all expression but the EoS by Trebble and Bishnoi, the "b"-coefficient is a component dependent constant. This expression may be rewritten to an equation for the compressibility factor Z:

$$Z = \frac{Pv}{RT} \tag{2}$$

$$Z^3 + \theta_1 z^2 + \theta_2 z + \theta_3 = 0 \tag{3}$$

Here, the parameters are:

$$\begin{aligned}
\theta_1 &= -B\left(m_1 + m_2\right) - B - 1 \\
\theta_2 &= B^2(m_1 m_2) + B^2(m_1 + m_2) + B(m_1 + m_2) + A \\
\theta_3 &= -B^3 m_1 m_2 - B^2 m_1 m_2 - AB
\end{aligned} \tag{4}$$

Here, A is:

$$A = \frac{a\alpha(T)P}{(RT)^2} \tag{5}$$

Table 1: Parameters used in the simulations

Year:	Name:	Functional form:
1873	Van der Waals	$P = \frac{RT}{v-b} - \frac{a}{v^2}$
1949	Redlich Kwong	$P = \frac{RT}{v-b} - \frac{a/T^{0.5}}{v(v+b)}$
1972	Soave Redlich Kwong	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v(v+b)}$
1976	Peng Robinson	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v(v+b)+b(v-b)}$
1980	Schmidt-Wensel	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v^2+(1+3c)bv-3cb^2}$
1982	Patel Teja	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v(v+b)+c(v-b)}$
1987	Yu-Lu	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v(v+b)+b(3v+c)}$
1987	Trebble-Bishnoi	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v^2+(b(T)+c)v-b(T)c-d^2}$

and B:

$$B = \frac{bP}{RT} \tag{6}$$

For three parameter cubic equations the C: is calculated as:

$$C = \frac{cP}{RT} \tag{7}$$

Table 2 shows how the constants/variables m_1 and m_2 varies with the EoS:

Table 2: m_1 and m_2 in the general cubic EoS

Name:	m_1	m_2
Van der Waals:	0	0
Redlich Kwong:	0	-1
Soave Redlich Kwong:	0	-1
Peng Robinson:	$-1+\sqrt{2}$	$-1-\sqrt{2}$
Schmidt-Wensel	$\frac{-1-3w+\sqrt{1+18w+9w^2}}{2}$	$\frac{-1-3w-\sqrt{1+18w+9w^2}}{2}$
Patel Teja:	$\frac{-b-c+\sqrt{b^2+2bc+c^2+4bc}}{2b}$	$\frac{-b-c-\sqrt{b^2+2bc+c^2+4bc}}{2b}$
Yu-Lu	$\frac{-c-3b+\sqrt{c^2+2bc+9b^2}}{2b}$	$\frac{-c-3b-\sqrt{c^2+2bc+9b^2}}{2b}$
Trebble-Bishnoi	$\frac{-b(T)-c+\sqrt{b(T)^2+6b(T)c+c^2+4d}}{2b(T)}$	$\frac{-b(T)-c-\sqrt{b(T)^2+6b(T)c+c^2+4d}}{2b(T)}$

The variables a, b c are constants in all but the last EoS, where b is temperature dependent. For all but the Redlich Kwong EoS, a and b have the following functional form:

$$a = \Omega_{a,i}\frac{R^2T_c^2}{P_c}$$
$$b = \Omega_{b,i}\frac{RT_c}{P_c} \tag{8}$$

In the first four EoS in Tab. 1, $\Omega_{a,i}$ and $\Omega_{b,i}$ are constants common for all the components, the EoS by Schmidt and Wensel has a more complicated expression for the factors, and in the EoS by

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Patel-Teja a third degree polynomial in the acentric factor has to be solved for each component at initialization. Note that for the two-parameter cubic EoS a and b are chosen to satisfy the following two equations:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \tag{9}$$

For a 3-parameter cubic equation of state the parameter c is also defined:
For Patel-Teja:

$$c = \Omega_{c,i}\frac{RT_c}{P_c} \tag{10}$$

For Schmidt and Wenzel the acentric factor ω is used for the parameter c

$$c = \omega \tag{11}$$

Where the critical compressibility $Z_{c,i}$ is treated as a parameter that can be fitted using the third equation:

$$\left(\frac{P_c V_c}{RT_c}\right) = Z_c \tag{12}$$

The frequently used form by Soave for the α-parameter is:

$$\alpha\left(T,\omega\right) = \left[1 + m\left(\omega\right)\left[1 - T_R^{0.5}\right]\right]^2 \tag{13}$$

This expression is used also by Peng and Robinson, Schmidt and Wenzel and Patel and Teja. To further improve the α-parameter, the following subject has received attention in the literature:

For the 3-parameter cubic EOS of Patel and Teja the component specific $Z_{c,i}$ and an m_i is provided in addition to the two general terms:

$$
\begin{aligned}
Z_c &= 0.329032 - 0.076799\omega + 0.0211947\omega^2 \\
m &= 0.452413 + 1.30982\omega - 0.295937\omega^2
\end{aligned}
\tag{14}
$$

- Vapour-pressures of any fluid, also polar should be well predicted.

- The behavior of the α-parameter in the supercritical region should be improved.

- Limitations at low reduced temperatures and large acentric factors should be overcome.

Many expressions have been suggested, such as the expression by Stryjek and Vera which requires an additional parameter for each component, k_1 and a function k_0 dependent of the component acentric factor.

$$\alpha\left(T,\omega\right) = \left(1 + \left(k_0(\omega) + k_1(1 - T_r^{0.5})/0.7 - T_r\right)\right)\left(1 - T_r^{0.5}\right)\right)^2 \tag{15}$$

The α-parameter should always be positive, decrease monotonically with pressure and reach 0 at infinite temperature. The form proposed by Soave becomes negative for some supercritical temperature and then increases. To give a qualitatively correct α-function, exponential functions could be used, such as in an three parameter EoS by Yu and Lu.

Van der Waals EoS is limited to uses one constant parameter accounting for the interaction between the components. This is the critical compressibility and it fixed to 0.375 for all components. The EoS by Redlich Kwong gave better description at higher pressure using the critical compressibility fixed to 0.333 for all components.

The temperature dependence of the attractive term, a_p (a product of a temperature,acentric factor- dependent α and a), was improved by Soave in 1972. The parameter is also correlated

with the acentric factor through the term m in eq. 13, to include component dependencies. Still as in Redlich Kwong, the critical compressibility is 0.333 for all components, and molar-volumes are typically overestimated. Peng Robinson changed the expression of the second term in the pressure relation in Eq. 1. This improved the volume predictions, but makes PR under-predict the saturation pressure of some fluids.

The α-term is treated as a separate function in the core of the library where also the analytical derivatives are developed.

3.1 Necessary functions for 3-parameter cubic equations of state

A modern flexible thermodynamic library should be able to calculate important state functions and derivatives of 3-parameter cubic equations of state, since these are frequently used in a large variety of applications, such as in hydrate formation predictions. In this section, it will be described how this can be accomplished. the content in this section is a modified version of the note by G. Owren and I.S. Melaaen from 1996 [3], adapted for 3-parameter cubic equations of state. We will restrict ourselves to mixing rules for the parameters b and c that only depend on composition.

3.2 The necessary state functions

State functions which any decent thermodynamic package should be able to calculate are the compressibility factor, z, the enthalpy, h, the entropy, s, and the fugacity coefficients $\phi = f/P$. To calculate the three last, the residual Helmholtz energy, $Y = Y_{ig} + Y_{Res}$, can be used as the starting point:

$$Y_{Res}(T, V, N) = \int_V^\infty \left(P - \frac{NRT}{V} \right) dV \tag{16}$$

$$Y_{Res}(T, P, N) = \int_V^\infty \left(P - \frac{NRT}{V} \right) dV - NRT \ln(Z) \tag{17}$$

A pressure function from a cubic equation of state is explicit in density and temperature and it can often be integrated analytically. Using the reduced Helmholtz function, $F \equiv A/(RT)$, one obtains:

$$F_{Res}(T, V, N) = \int_V^\infty \left(\frac{P}{RT} - \frac{N}{V} \right) dV = N \left[\ln \left(\frac{V}{V - B} \right) - \frac{A}{(m_1 - m_2) BRT} \cdot \ln \left(\frac{V - m_2 B}{V - m_1 B} \right) \right] \tag{18}$$

The residual entropy can be calculated from F partial derivatives of F together with the compressibility factor:

$$S_{Res} = \left(\frac{\partial Y_{Res}}{\partial T} \right)_{V, N_i} = (-R) \cdot \left(T \left(\frac{\partial F}{\partial T} \right)_{P, N_j} + F + N \ln(Z) \right) \tag{19}$$

Moreover, the residual enthalpy is:

$$H_{Res} = Y_{Res} - TS_{Res} + RT(Z - 1) \tag{20}$$

Using ideal gas at a pressure P as the reference, the fugacity coefficient is:

$$\ln(\phi) = \ln \left(\frac{f_i}{P} \right) = \frac{\mu_{i,Res}}{RT} = \frac{1}{RT} \left(\frac{\partial Y_{Res}}{\partial N_i} \right)_{T, P, N_j} = \left(\frac{\partial F}{\partial N_i} \right)_{T, P, N_j} - \ln(Z) \tag{21}$$

The necessary functions to do flash-calculations with numerical derivatives are given above, combined with $(\partial F/\partial T)_{P,N,i}$ for entropy an $(\partial F/\partial N_i)_{T,P}$ for the fugacities. Since a pressure

function is the most common way to represent cubic equations of state, and the F-function plays an important role in the necessary state function, analytical derivatives will be given below, first for the reduced Helmholtz-function and then for the pressure

3.3 The reduced Helmholtz-function - simplified

The reduced residual Helmholtz free energy function, F, for a general cubic equation of state with two or three parameters (A,B and C) can be expressed as

$$F = F(N, T, V, D, B, C) = -Ng(V, B) - \frac{A(T)}{T} f(V, B, C) \tag{22}$$

where g is defined as:

$$g = \ln(1 - \frac{B}{V}) = \ln(V - B) - \ln V \tag{23}$$

and f is defined as:

$$f = \frac{1}{R \cdot B \left(m_1 - m_2 \right)} \ln \frac{V - m_2 B}{V - m_1 B} \tag{24}$$

in the f-function the m_1 and m_2 can both be functions of B and the third parameter C. In some cases B and C can be functions of temperature also.

In the implementation, the following short-functions are used:

$$n_1(V, B, C) = V - m_1 B \tag{25}$$
$$n_2(V, B, C) = V - m_2 B \tag{26}$$
$$n(V, B) = V - B \tag{27}$$
$$m(B, C) = m_1 - m_2 \tag{28}$$
$$h(V, B, C) = \ln\left(\frac{n_2}{n_1}\right) = \ln n_2 - \ln n_1 \tag{29}$$

Then the f and g-function can be expressed as:

$$f = \frac{h}{m \cdot R \cdot B} \tag{30}$$
$$g = \ln n - \ln V \tag{31}$$

The total number of moles N is:

$$N = \sum_i N_i \tag{32}$$

The temperature dependent parameter A is defined as $N^2 a_{mix}$, $B = \sum_i N_i b_{ii}$ and $C = \sum_i c_{ii}$. The mixing rules are discussed further in section 3.5.1

3.3.1 Partial derivatives of F for calculation of thermodynamic properties

The partial derivatives required for the various thermodynamic properties are listed next.

For making the derived it is asumed A and B is a function of composition and temperaturee where C is only a function of composition. This can be written:

$$F = F\left(N, T, A(N, T), B(N, T), C(N)\right) \tag{33}$$

First order derivatives

$$\left(\frac{\partial F}{\partial N_i}\right)_{T,V,Nj} = F_N + F_A \cdot A_i + F_B \cdot B_i + F_C \cdot C_i \tag{34}$$

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$$\left(\frac{\partial F}{\partial T}\right)_{V,\mathbf{N}} = F_T + F_A \cdot A_T + F_B \cdot B_T \tag{35}$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,\mathbf{N}} = F_V \tag{36}$$

Second order derivatives

The development of the second order derived is not straight forward and the development of the formula is of that reason shown:

$$
\begin{aligned}
\left(\frac{\partial^2 F}{\partial T \partial N_i}\right)_{V,N_j} &= \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial N_i}\right) = \frac{\partial}{\partial T}\left(F_N + F_A A_i + F_B B_i + F_C C_i\right)\\
&= \frac{\partial F_n}{\partial T} + F_A \frac{\partial A_i}{\partial T} + A_i \frac{\partial F_A}{\partial T} + F_B \frac{\partial B_i}{\partial T} + B_i \frac{\partial F_B}{\partial T} + C_i \frac{\partial F_C}{\partial T}\\
&= F_{NT} + F_{NA} A_T + F_{NB} B_T\\
&\quad + F_A A_{iT} + A_i\left(F_{AT} + F_{AA} A_T + F_{AB} B_T\right)\\
&\quad + F_B B_{iT} + B_i\left(F_{BT} + F_{BA} A_T + F_{BB} B_T\right)\\
&\quad + C_i\left(F_{CT} + F_{CA} A_T + F_{CB} B_T\right)
\end{aligned}
\tag{37}
$$

$$
\begin{aligned}
\left(\frac{\partial^2 F}{\partial N_j \partial N_i}\right)_{T,V} &= \frac{\partial}{\partial N_j}\left(\frac{\partial F}{\partial N_i}\right) = \frac{\partial}{\partial N_j}\left(F_N + F_A A_i + F_B B_i + F_C C_i\right)\\
&= \frac{\partial F_n}{\partial N_j} + F_A \frac{\partial A_i}{\partial N_j} + A_i \frac{\partial F_A}{\partial N_j} + F_B \frac{\partial B_i}{\partial N_j} + B_i \frac{\partial F_B}{\partial N_j} + C_i \frac{\partial F_C}{\partial N_j}\\
&= F_{NN} + F_{NA} A_j + F_{NB} B_j + F_{NC} C_j\\
&\quad + F_A A_{ij} + A_i\left(F_{AN} + F_{AA} A_j + F_{AB} B_j + F_{AC} C_j\right)\\
&\quad + F_B B_{ij} + B_i\left(F_{BN} + F_{BA} A_j + F_{BB} B_j + F_{BC} C_j\right)\\
&\quad + F_C C_{ij} + C_i\left(F_{CN} + F_{CA} A_j + F_{CB} B_j + F_{CC} C_j\right)
\end{aligned}
\tag{38}
$$

It is her used that $F_{NN} = F_{NA} = F_{NC} = 0$ and that therm is then not incldued in the code

$$
\begin{aligned}
\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} &= \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T}\left(F_T + F_A A_T + F_B B_T\right)\\
&= \frac{\partial F_T}{\partial T} + F_A \frac{\partial A_T}{\partial T} + A_T \frac{\partial F_A}{\partial T} + F_B \frac{\partial B_T}{\partial T} + B_T \frac{\partial F_B}{\partial T}\\
&= F_{TT} + F_{TA} A_T + F_{TB} B_T\\
&\quad + F_A A_{TT} + A_T\left(F_{AT} + F_{AA} A_T + F_{BA} B_T\right)\\
&\quad + F_B B_{TT} + B_T\left(F_{BT} + F_{BA} A_T + F_{BB} B_T\right)\\
&= F_{TT} + 2 F_{TA} A_T + 2 F_{TB} B_T\\
&\quad + F_A A_{TT} + F_B B_{TT}\\
&\quad + F_{AA} A_T^2 + 2 F_{AB} A_T B_T + F_{BB} B_T^2
\end{aligned}
\tag{39}
$$

The partial derivatives of the F-function is listed next.

3.3.2 The partial derivatives of F-function

First order derivatives

$$F_N = -g \tag{40}$$

$$F_A = -\frac{f}{T} \tag{41}$$

$$F_B = -g_B - \frac{A}{T}f_B \tag{42}$$

$$F_C = -\frac{A}{T}f_C \tag{43}$$

$$F_T = \frac{A}{T^2}f \tag{44}$$

$$F_{AB} = -\frac{f_B}{T} \tag{45}$$

$$F_{AC} = -\frac{f_C}{T} \tag{46}$$

$$F_{AT} = \frac{f}{T^2} \tag{47}$$

$$F_{BB} = -g_{BB} - \frac{A}{T}f_{BB} \tag{48}$$

$$F_{BC} = -\frac{A}{T}f_{BC} \tag{49}$$

$$F_{BT} = \frac{A}{T^2}f_B \tag{50}$$

$$F_{CT} = \frac{A}{T^2}f_C \tag{51}$$

$$F_{CC} = -\frac{A}{T} f_{CC} \tag{52}$$

$$F_{TT} = -2.0 \frac{F_T}{T} \tag{53}$$

$$F_V = -g_V - \frac{A}{T} f_V \tag{54}$$

$$F_{NV} = -g_V \tag{55}$$

$$F_{NB} = -g_B \tag{56}$$

$$F_{VT} = \frac{A}{T^2} f_V \tag{57}$$

$$F_{VV} = -g_{VV} - \frac{A}{T} f_{VV} \tag{58}$$

$$F_{VA} = -\frac{f_V}{T} \tag{59}$$

$$F_{VB} = -g_{VB} - \frac{A}{T} f_{VB} \tag{60}$$

$$F_{VC} = -\frac{A}{T} f_{VC} \tag{61}$$

The following derivatives are zero: F_{NN}, F_{NT}, F_{NA}, F_{AA} and F_{NC}

3.3.3 Derivatives of the helper functions f and g

With the help of the notations described above:

$$f_V = \frac{h_V}{m \cdot B \cdot R} \tag{62}$$

$$f_B = \frac{h_B}{m \cdot B \cdot R} - \frac{f}{B} - \frac{f \cdot m_B}{m} \tag{63}$$

$$f_C = \frac{h_C}{m \cdot B \cdot R} - \frac{f \cdot m_C}{m} \tag{64}$$

$$f_{VV} = \frac{h_{VV}}{m \cdot B \cdot R} \tag{65}$$

$$f_{VB} = \frac{1}{m \cdot B \cdot R} \left(h_{VB} - \frac{h_V}{m} m_B - \frac{h_V}{B} \right) \tag{66}$$

$$f_{VC} = \frac{1}{m \cdot B \cdot R} \left(h_{VC} - \frac{h_V}{m} m_C \right) \tag{67}$$

$$f_{BB} = \frac{1}{m \cdot B \cdot R} \left[h_{BB} - R \left(2 f_B \left(m + m_B \right) + f \left(m_B + m_{BB} \right) \right) \right] \tag{68}$$

$$f_{BC} = \frac{1}{m \cdot B \cdot R} \left(h_{BC} - \frac{h_B m_C + h_C m_B + h m_{BC}}{m} + \frac{2 h m_B m_C}{m^2} - \frac{h_C}{B^2} \right) \tag{69}$$

$$f_{CC} = \frac{1}{m \cdot B \cdot R} \left(h_{CC} - \frac{2 h_C m_C + h m_{CC}}{m} + \frac{2 h m_C^2}{m^2} \right) \tag{70}$$

$$g_V = \frac{1}{n} - \frac{1}{V} \tag{71}$$

$$g_B = -\frac{1}{n} \tag{72}$$

$$g_{VV} = -\frac{1}{n^2} + \frac{1}{V^2} \tag{73}$$

$$g_{VB} = \frac{1}{n^2} \tag{74}$$

$$g_{BB} = -g_{VB} \tag{75}$$

The partial derivatives of h, m, n_1, n_2 and n are listed in the appendix for completeness.

3.4 The pressure function with derivatives

The pressure and the derivatives are often needed and although the pressure with the derivatives are directly described from the F-function in the previous section, it is convenient to have these directly available.

With the mixing parameters scaled to: $A = N^2 a\alpha(T)$ and $B = Nb$. the equation in 1 may be rewritten as:

From the F-function the pressure is expressed as:

$$P = R \cdot T \left(-F_V + \frac{1}{V} \right) \tag{76}$$

or

$$P = \frac{NRT}{V - B} + \frac{A}{(V - Bm_1)(V - Bm_2)} \tag{77}$$

With the short-functions used in the implementation

$$p = \frac{R \cdot T}{n} - \frac{A}{n_1 \cdot n_2} \tag{78}$$

where (repeated):

$$
\begin{aligned}
n &= V - B \\
n1 &= V - m_1 B \\
n2 &= V - m_2 B
\end{aligned}
$$

3.4.1 The derivatives of $P(N,V,T,A,B,C)$

With $a_p = a\alpha(T)$, the derivatives of the pressure with respect to the total number of moles, N, the volume V, the temperature, T, and the parameters A, B and C are:

$$N \cdot P_N = N \cdot \frac{\partial P}{\partial N} = \frac{R \cdot T}{V - B} \tag{79}$$

$$N \cdot P_V = \frac{-RT}{(V - B)^2} + a_p \frac{n_1 + n_2}{(n_1 \cdot n_2)^2} \tag{80}$$

$$N^2 P_A = N^2 \cdot \frac{\partial P}{\partial A} = \frac{-1}{n_1 \cdot n_2} \tag{81}$$

$$N \cdot P_B = N \cdot \frac{\partial P}{\partial B} = \frac{RT}{(V - B)^2} - a_p \cdot \frac{(m_1 + B \cdot m_{1,B}) \cdot n_2 + (m_2 + B \cdot m_{2,B}) \cdot n_2}{(n_1 \cdot n_2)^2} \tag{82}$$

$$N \cdot P_C = N \cdot \frac{\partial P}{\partial C} = -R \cdot A \cdot F_{VC} \tag{83}$$

$$P_T = \frac{\partial P}{\partial T} = \frac{T}{V - B} \tag{84}$$

3.4.2 The derivatives of $\mathbf{P}(T,V,N_i)$

Assuming that m_1 and m_2 are both functions of B and an additional parameter C, the pressure derivatives are:

$$\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} = P_N + P_A \cdot A_i + P_B \cdot B_i + P_C \cdot C_i \tag{85}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,\mathbf{N}} = P_V \tag{86}$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,\mathbf{N}} = P_T + P_A \cdot A_T + P_B \cdot B_T + P_C \cdot C_T \tag{87}$$

Without temperature dependency in B and C the terms B_T and C_T becomes zero.

3.5 Mixing rules

With the expression for the pressure and f-function derivatives at hand, we have still not defined the composition derivatives of the mixing rules which will dictate the composition dependency of the m_1 and m_2 parameters. This section contains these derivatives for both the standard and the Huron-Vidal mixing rules, and also the composition derivatives of, m_1 and m_2 for the 3-parameter cubic EoS by Schmidt and Wensel described previously.

3.5.1 Standard mixing rules

For the parameters a_p and B, the mixing rules are:

$$B = \sum_i x_i b_i \tag{88}$$

$$A = \sum_i \sum_j x_i x_j a_{p,ij} \tag{89}$$

$$a_{p,ij} = \sqrt{a_{p,i} a_{p,j}} \left(1 - k_{ij}\right) \tag{90}$$

If we make the a and b not composition dependent, $A = N^2 a$ and $B = Nb$ this results in the following composition derivatives:

$$\frac{1}{N} A_i = \frac{1}{N} \frac{\partial A}{\partial N_i} = 2 \sum_j x_j a_{p,ij} \tag{91}$$

$$\frac{1}{N} A_{iT} = \frac{1}{N} \frac{\partial^2 A}{\partial N_i \partial T} = 2 \sum_j x_j \frac{da_{p,ij}}{dT} \tag{92}$$

$$\frac{1}{N^2} A_T = \frac{1}{N^2} \frac{\partial A}{\partial T} = \frac{1}{2} \sum_i x_i \frac{A_{iT}}{N} \tag{93}$$

$$\frac{1}{N^2} A_{TT} = \frac{1}{N^2} \frac{\partial^2 A}{\partial T^2} = \sum_i x_i \sum_j x_j \frac{\partial^2 a_{p,ij}}{\partial T^2} \tag{94}$$

$$B_i = \frac{\partial B}{\partial N_i} = b_i \tag{95}$$

$$\frac{da_{p,ij}}{dT} = (1 - k_{ij}) \cdot \frac{1}{2\sqrt{a_{p,i} a_{p,j}}} \cdot \left(a_{p,i} \frac{da_{p,j}}{dT} + a_{p,j} \frac{da_{p,i}}{dT} \right) \tag{96}$$

$$\frac{d^2 a_{p,ij}}{dT^2} = \frac{1 - k_{ij}}{2} \cdot \left(\frac{2 \frac{da_{p,i}}{dT} \frac{da_{p,j}}{dT} + a_{p,i} \frac{d^2 a_{p,j}}{dT^2} + a_{p,j} \frac{d^2 a_{p,i}}{dT^2}}{\sqrt{a_{p,i} a_{p,j}}} - \frac{\left(a_{p,i} \frac{da_{p,j}}{dT} + a_{p,j} \frac{da_{p,i}}{dT} \right)^2}{2\sqrt{a_{p,i} a_{p,j}} a_{p,i} a_{p,j}} \right) \tag{97}$$

<center>🟫 **Thermotools memo**</center>

The derivatives of the m_1 and m_2 functions

For Schmidt and Wensel:

$$\left(\frac{\partial m_1}{\partial C}\right) = -\frac{3}{2} + \frac{9 + 9C}{2\sqrt{1 + 18C + 9C^2}} \tag{98}$$

$$\left(\frac{\partial m_2}{\partial C}\right) = -\frac{3}{2} - \frac{9 + 9C}{2\sqrt{1 + 18C + 9C^2}} \tag{99}$$

$$\left(\frac{\partial^2 m_1}{\partial C^2}\right) = \frac{9}{2\sqrt{1 + 18C + 9C^2}} - \frac{9 + 9C}{4\left(1 + 18C + 9C^2\right)^{1.5}} \tag{100}$$

$$\left(\frac{\partial^2 m_2}{\partial C^2}\right) = -\left(\frac{\partial^2 m_1}{\partial C^2}\right) \tag{101}$$

For Patel-Teja Equation of state:
With m_1 and m_2 defined as:

$$m_1 = \frac{-B - C + \sqrt{D}}{2B} \tag{102}$$

$$m_2 = \frac{-B - C - \sqrt{D}}{2B} \tag{103}$$

With: $D = B^2 + 6 \cdot B \cdot C + C^2$
The derivatives are the following:

$$\left(\frac{\partial m_1}{\partial B}\right) = -\frac{C \cdot \left(3 \cdot B - \sqrt{D} + C\right)}{2\sqrt{D}B^2} \tag{104}$$

$$\left(\frac{\partial m_2}{\partial B}\right) = \frac{C \cdot \left(3 \cdot B + \sqrt{D} + C\right)}{2\sqrt{D}B^2} \tag{105}$$

$$\left(\frac{\partial m_1}{\partial C}\right) = \frac{3 \cdot B + C - \sqrt{D}}{2\sqrt{D}B} \tag{106}$$

$$\left(\frac{\partial m_2}{\partial C}\right) = -\frac{3 \cdot B + C + \sqrt{D}}{2\sqrt{D}B} \tag{107}$$

The second order derivatives of B and C
With the help of the following definitions:

$$D = B^2 + 6 \cdot B \cdot C + C^2 \tag{108}$$
$$F = 3B + C \tag{109}$$
$$G = B^2 + 5 \cdot B \cdot C + 3C^2 \tag{110}$$
$$H = B^3 \cdot D \cdot \sqrt{D} \tag{111}$$

the second order derivatives are:

$$\left(\frac{\partial^2 m_1}{\partial B^2}\right) = \frac{C\left(3B \cdot G - D\sqrt{D} + C^3\right)}{H} \tag{112}$$

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$$\left(\frac{\partial^2 m_2}{\partial B^2}\right) = -\frac{C\left(3B\cdot G + D\sqrt{D} + C^3\right)}{H} \tag{113}$$

$$\left(\frac{\partial^2 m_1}{\partial C^2}\right) = -\frac{F^2 - D}{2B\cdot D\sqrt{D}} \tag{114}$$

$$\left(\frac{\partial^2 m_2}{\partial C^2}\right) = -\left(\frac{\partial^2 m_1}{\partial C^2}\right) \tag{115}$$

The cross derivatives are:

$$\left(\frac{\partial^2 m_1}{\partial B\partial C}\right) = -\frac{\left(E - \sqrt{D}\right)\cdot\left(B\left(B+3C\right) - C\sqrt{D}\right)}{2D\sqrt{D}B^2} \tag{116}$$

$$\left(\frac{\partial^2 m_2}{\partial B\partial C}\right) = \frac{\left(E + \sqrt{D}\right)\cdot\left(B\left(B+3C\right) + C\sqrt{D}\right)}{2D\sqrt{D}B^2} \tag{117}$$

3.5.2 Mixing rule for B and C in the 3-parameter cubic EOS

The standard mixing rules for in Schmidt and Wensel:

$$C = \frac{\sum_r x_r w_r b_r^{0.7}}{\sum_k x_k b_k^{0.7}} \tag{118}$$

Introducing the two variables γ_1 and γ_2 as:

$$\gamma_1 = \sum_r x_r w_r b_r^{0.7} \tag{119}$$

$$\gamma_2 = \sum_k x_k b_k^{0.7} \tag{120}$$

Gives the following derivatives:

$$N\cdot C_i = N\cdot\frac{dc}{dN_i} = \frac{b_i^{0.7}}{\gamma_2}\left(w_i - \frac{\gamma_1}{\gamma_2}\right) \tag{121}$$

and

$$N^2\cdot C_{ij} = N^2\cdot\left(\frac{\partial^2 C}{\partial N_i N_j}\right) = -\frac{b_i^{0.7}b_j^{0.7}}{\gamma_2^2}\left(w_i + w_j - 2\frac{\gamma_1}{\gamma_2}\right) \tag{122}$$

The standard mixing rule for Patel Teja:

$$C = N\cdot\sum_i x_i c_i \tag{123}$$

and

$$B = N\cdot\sum_i x_i b_i \tag{124}$$

Gives the following derivatives:

$$N \cdot C_i = N \cdot \left(\frac{\partial C}{\partial N_i} \right) = c_i \tag{125}$$

and

$$N \cdot B_i = N \cdot \left(\frac{\partial B}{\partial N_i} \right) = b_i \tag{126}$$

The second derivatives B_{ij} and C_{ij} are zero.

3.5.3 The Huron Vidal mixing rule

To have the Huron-Vidal mixing rule as a equivalent mixing rule as the standard mixing rule by van der Waals in our thermodynamic package, analytical derivatives have to be supplied. The Huron-Vidal mixing rule is for the mixture parameter a:

$$a = b \left[\sum_{z=1}^{N} \left(x_z \frac{a_z}{b_z} \right) - \frac{G_\infty^E}{\ln 2} \right] \tag{127}$$

(Note: The a_z-parameter is here the a_p parameter described earlier as $\alpha(T)a$) Here, the excess Gibbs energy at infinite pressure is:

$$G_\infty^E = RT \sum_{z=1}^{N} x_z \frac{\sum_{r=1}^{N} \tau_{rz} b_r x_r C_{rz}}{\sum_{k=1}^{N} b_k x_k C_{kz}} \tag{128}$$

Moreover, the other parameters are:

$$\tau_{rz} = \frac{\Delta g_{rz}}{RT} \tag{129}$$

$$C_{rz} = \exp\left(-\alpha_{rz} \tau_{rz} \right) \tag{130}$$

Here, α_{ji} are typically constants, while Δg_{ji} are either first degree polynomials in the temperature (HV1):

$$\tau_{rz} = \frac{1}{R} \left(\frac{a_{rz}}{T} + b_{rz} \right) \tag{131}$$

or second degree polynomials (HV2):

$$\tau_{rz} = \frac{1}{R} \left(\frac{a_{rz}}{T} + b_{rz} + c_{rz} T \right) \tag{132}$$

For interactions between non-polar components were specific values for α and τ has not been fitted, the mixing-rule falls back to the standard Van der Waals mixing rule with one interaction parameter k_{ij} if the excess energy parameters are chosen as:

$$\alpha_{ij} = 0 \tag{133}$$

$$g_{ii} = \frac{a_i}{b_i} \Delta \tag{134}$$

$$g_{ji} = -2 \frac{\sqrt{b_i b_j}}{b_i + b_j} \sqrt{g_{ii} g_{jj}} \left(1 - k_{ij} \right) \tag{135}$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{136}$$

($\Delta = \ln 2$ for SRK, 1.0 for VdW and 0.623 for the PR EOS)

The 1st and 2nd derivative of the τ-function are also developed. Using the above equations with the Huron-Vidal mixing rule, is fully consistent and equivalent to using SRK with VdW mixing rule. This is very convenient to use for a mixture containing polar and non-polar substances avoiding too much "bookkeeping" in the implementation.

The temperature derivative, $\frac{dA}{dT}$ (checked numerically)

The overall expression:

$$\frac{1}{N^2}\frac{\partial A}{\partial T} = b\left[\sum_{z=1}^{N}\left(x_z\frac{1}{b_z}\right)\frac{\partial a_z}{\partial T} - \frac{1}{\ln 2}\frac{\partial G_\infty^E}{\partial T}\right] \tag{137}$$

and then:

$$\begin{aligned}
\frac{\partial G_\infty^E}{\partial T} &= R\sum_{z=1}^{N} x_z\frac{\sum_{r=1}^{N}\tau_{rz}b_r x_r C_{rz}}{\sum_{k=1}^{n}b_k x_k C_{kz}} + \\
&RT\sum_{z=1}^{N} x_z\left(\frac{\sum_{r=1}^{N}\tau_{rz}b_r x_r C_{rz}}{\left(\sum_{k=1}^{N}b_k x_k C_{kz}\right)^2}\sum_{k=1}^{N}b_k x_k \alpha_{kz}C_{kz}\frac{\partial \tau_{kz}}{\partial T}\right) + \\
&RT\sum_{z=1}^{N} x_z\left(\frac{\sum_{r=1}^{N}\frac{\partial \tau_{rz}}{\partial T}b_r x_r C_{rz} - \alpha_{rz}\tau_{rz}\frac{\partial \tau_{rz}}{\partial T}b_r x_r C_{rz}}{\sum_{k=1}^{N}b_k x_k C_{kz}}\right)
\end{aligned} \tag{138}$$

The first and second temperature derivatives of τ (HV1):

$$\frac{\partial \tau_{rz}}{\partial T} = \frac{1}{R}\left(-\frac{a_{rz}}{T^2}\right) \qquad\qquad \frac{\partial^2 \tau_{rz}}{\partial T^2} = \frac{1}{R}\left(\frac{2a_{rz}}{T^3}\right) \tag{139}$$

The first and second temperature derivatives of τ (HV2):

$$\frac{\partial \tau_{rz}}{\partial T} = \frac{1}{R}\left(-\frac{a_{rz}}{T^2} + c_{rz}\right) \qquad\qquad \frac{\partial^2 \tau_{rz}}{\partial T^2} = \frac{1}{R}\left(\frac{2a_{rz}}{T^3}\right) \tag{140}$$

The composition derivative, $\frac{dA}{dN_i}$ (checked numerically)

The overall expression:

$$\frac{1}{N}\frac{\partial A}{\partial N_i} = b_i\cdot\left[\sum_{z=1}^{N}\left(x_z\frac{a_z}{b_z}\right) - \frac{G_\infty^E}{\ln 2}\right] + b\left[\frac{a_i}{b_i} - \frac{1}{\ln 2}\cdot\frac{\partial\left(G_\infty^E\cdot N\right)}{\partial N_i}\right] \tag{141}$$

where:

$$\frac{\partial\left(G_\infty^E\cdot N\right)}{\partial N_i} = RT\cdot\left(\frac{\sum_{r=1}^{N}\tau_{ri}b_r x_r C_{ri}}{\sum_{k=1}^{N}b_k x_k C_{ki}} + \sum_{z=1}^{N}\frac{x_z\tau_{iz}b_i C_{iz}}{\sum_{k=1}^{N}b_k x_k C_{kz}} - \sum_{z=1}^{N}x_z b_i C_{iz}\frac{\sum_{r=1}^{N}\tau_{rz}b_r x_r C_{rz}}{\left(\sum_{k=1}^{N}b_k x_k C_{kz}\right)^2}\right) \tag{142}$$

The second degree composition derivative, $\frac{d^2A}{dN_i dN_j}$

The overall expression:

$$\frac{\partial^2 A}{\partial N_i \partial N_j} = b_i \cdot \left[\frac{a_j}{b_j} - \frac{1}{\ln 2} \frac{(G_\infty^E \cdot N)}{\partial N_j} \right] + b_j \left[\frac{a_i}{b_i} - \frac{1}{\ln 2} \cdot \frac{\partial (G_\infty^E \cdot N)}{\partial N_i} \right] - \frac{b \cdot N}{\ln 2} \cdot \frac{(\partial G_\infty^E \cdot N)}{\partial N_i \partial N_j} \quad (143)$$

where:

$$\frac{\partial^2 (G_\infty^E \cdot N)}{\partial N_i \partial N_j} \cdot \frac{N}{RT} = \frac{\tau_{ji} b_j C_{ji}}{\sum_k^N b_k x_k c_{ki}} - (b_j C_{ji}) \cdot \frac{\sum_{r=1}^N \tau_{ri} b_r x_r C_{ri} +}{\left(\sum_k^N b_k x_k C_{ki} \right)^2}$$

$$\frac{\tau_{ij} b_i c_{ij}}{\sum_k^N b_k x_k c_{kj}} - \sum_z^N x_z (b_j C_{jz}) \cdot \frac{\tau_{iz} b_i C_{iz}}{\left(\sum_k^N b_k x_k C_{kz} \right)^2} +$$

$$- (b_i C_{ij}) \cdot \frac{\sum_r^N \tau_{rj} b_r x_r C_{rj}}{\left(\sum_k^N b_k x_k C_{kj} \right)^2} - \sum_z^N x_z (b_i C_{iz}) \frac{\tau_{jz} b_j C_{jz}}{\left(\sum_k^N b_k x_k C_{kz} \right)^2} + 2 \sum_z^N x_z b_i b_j C_{iz} C_{jz} \frac{\sum_r^N \tau_{rz} b_r x_r C_{rz}}{\left(\sum_{k=1}^N b_k x_k C_{kz} \right)^3}$$

$$(144)$$

The second degree temperature derivative, $\frac{d^2 A}{dT^2}$ (checked numerically)

To write the expression of this derivative in a presentable form, the following helping variables, for the inner loops and their derivatives, will be used:

$$\gamma_1(z) = \sum_{r=1}^N \tau_{rz} b_r x_r C_{rz} \quad (145)$$

$$\gamma_2(z) = \sum_{k=1}^N b_k x_k C_{kz} \quad (146)$$

$$\gamma_3(z) = \sum_{k=1}^N b_k x_k \alpha_{kz} C_{kz} \frac{\partial \tau_{kz}}{\partial T} \quad (147)$$

$$\gamma_4(z) = \sum_{r=1}^n \frac{\partial \tau_{rz}}{\partial T} b_r x_r C_{rz} - \alpha_{rz} \tau_{rz} \frac{\partial \tau_{rz}}{\partial T} b_r x_r C_{rz} \quad (148)$$

$$\gamma_5(z) = \sum_{k=1}^N \left(b_k x_k C_{kz} (\alpha_{kz} \left(\frac{\partial^2 \tau_{kz}}{\partial T^2} - \alpha \frac{\partial \tau_{kz}}{\partial T})^2 \right) \right) \quad (149)$$

$$\gamma_6(z) = \sum_{r=1}^N \left(\frac{\partial^2 \tau_{rz}}{\partial T^2} b_r x_r C_{rz} - (\frac{\partial \tau_{rz}}{\partial T})^2 b_r x_r \alpha_{rz} C_{rz} - \alpha_{rz} (\frac{\partial \tau_{rz}}{\partial T})^2 b_r x_r C_{rz} - \right.$$
$$\left. \alpha_{rz} \tau_{rz} \frac{\partial^2 \tau_{rz}}{\partial T^2} b_r x_r C_{rz} + \alpha_{rz}^2 (\frac{\partial \tau_{rz}}{\partial T})^2 \tau_{rz} b_r x_r C_{rz} \right) \quad (150)$$

We recognize γ_3 as $-\frac{\partial \gamma_2}{\partial T}$, γ_4 as $\frac{\partial \gamma_1}{\partial T}$, γ_5 as $\frac{\partial \gamma_3}{\partial T}$ or $-\frac{\partial^2 \gamma_2}{\partial T}$ and γ_6 as $\frac{\partial \gamma_4}{\partial T}$ or $\frac{\partial^2 \gamma_1}{\partial T}$.
The overall expression:

$$\frac{1}{N^2} \frac{\partial^2 A}{\partial^2 T} = b \left[\sum_{z=1}^N \left(x_z \frac{1}{b_z} \right) \frac{\partial^2 a_z}{\partial T^2} - \frac{1}{\ln 2} \frac{\partial^2 G_\infty^E}{\partial T^2} \right] \quad (151)$$

where:

$$\frac{\partial^2 G_\infty^E}{\partial T^2} = 2R \cdot \sum_{z=1}^{N} x_z \left(\frac{\gamma_1 \gamma_3}{\gamma_2^2} + \frac{\gamma_4}{\gamma_2} \right) + RT \cdot \sum_{z=1}^{N} x_z \left(\frac{2\gamma_1 \gamma_3^2}{\gamma_2^3} \right)$$
$$+ RT \cdot \sum_{z=1}^{N} x_z \left(\frac{2\gamma_4 \gamma_3 + \gamma_1 \gamma_5}{\gamma_2^2} \right) + RT \cdot \sum_{z=1}^{N} x_z \left(\frac{\gamma_6}{\gamma_2} \right) \tag{152}$$

The second degree composition, temperature derivative, $\frac{d^2 A}{dN_i dT}$

The overall expression:

$$\frac{1}{N} \frac{\partial A}{\partial N_i \partial T} = b_i \left[\sum_{z=1}^{N} \left(\frac{x_z}{b_z} \right) \cdot \frac{\partial a_z}{\partial T} - \frac{1}{\ln(2)} \frac{\partial G_\infty^E}{\partial T} \right] + b \left[\frac{1}{b_i} \frac{\partial a_i}{\partial T} - \frac{1}{\ln(2)} \frac{(G_\infty^E \cdot N)}{\partial N_i \partial T} \right] \tag{153}$$

$$\frac{\partial^2 G_\infty^E \cdot N}{\partial N_i \partial T} = \frac{1}{T} \cdot \frac{\partial (G_\infty^E \cdot N)}{\partial N_i} +$$
$$RT \cdot \left(\frac{\gamma_1(i)\gamma_3(i)}{\gamma_2(i)^2} + \frac{\gamma_4(i)}{\gamma_2(i)} + \sum_{z=1}^{N} \frac{x_z b_i \left(\frac{\partial \tau_{iz}}{\partial T} C_{iz} - \alpha_{iz} \frac{\partial \tau_{iz}}{\partial T} C_{iz} \tau_{iz} \right)}{\gamma_2(z)} + \sum_{z=1}^{N} \frac{x_z b_i \tau_{iz} C_{iz} \gamma_3(z)}{\gamma_2(z)^2} \right.$$
$$\left. + \sum_{z=1}^{N} x_z b_i \alpha_{iz} \frac{\partial \tau_{iz}}{\partial T} C_{iz} \cdot \frac{\gamma_1(z)}{\gamma_2(z)^2} - \sum_{z=1}^{N} x_z b_i C_{iz} \frac{\gamma_4(z)}{\gamma_2(z)^2} - 2 \sum_{z=1}^{N} x_z b_i C_{iz} \frac{\gamma_1(z)\gamma_3(z)}{\gamma_2(z)^3} \right) \tag{154}$$

4 Conclusion and future work

To be prepared for many of the new challenged arising in CCS-thermodynamics, such as solid formation, the existence of several liquid phases and many other scientifically interesting topics, the development of a new flexible workbench for thermo-physical properties has been initiated. The flexible workbench has been called ThermoPack, and will be implemented in FORTRAN 95 with mercurial as a version-control tool. In this memo, the computational structure of the program has been explained, starting with the input data structure and continuing with the driver routines which explains how a minimum of functions are chosen as a basis. Other useful thermodynamic functions are calculated through an utility module, and these functions with derivatives are supplied to the core routines which can be flash-calculations, density calculations and much more. Automatic numerical derivation can be performed on the necessary state functions with an input flag=2, and analytical derivatives are given with an input flag=1 (only if analytic derivatives are available). In the next sections, the mathematical framework for implementing state-of-the-art three-parameter cubic equations of state with analytical derivatives has been explained. The analytical derivatives have been given for standard and Huron-Vidal mixing rules, and for the three-parameter equation of state by Schmidt and Wensel.

- The mathematical framework for three-parameter cubic EoS described in this memo should be implemented in ThermoPack. Currently, only two-parameter cubic EoS are available. *D*ONE

- The three-parameter cubic EoS Schmidt-Wensel and the promising EoS; Patel-Teja, should be implemented and tested in the new framework to see if 3-parameter EoS better describe the behavior of CO_2-mixtures than the standard 2-parameter cubic EoS SRK and Peng-Robinson. *D*ONE (but more testing is required)

- More utility functions for adding and administration of the component, correlation and mixing rules database should be implemented.

Nomenclature

Roman symbols

a	Constant in SRK and PR EOS, $(Pa \cdot m^6)$
a_p	Constant in cubic EoS, product of temperature dependent,α and a. $(Pa \cdot m^6/mol^2)$
A	Constant in cubic EoS, $(Pa \cdot m^6)$
b	Constant in cubic EoS, (m^3/mol)
B	Constant in cubic EoS, (m^3)
c	Constant in three-parameter cubic EoS, (m^3/mol)
C	Constant in three-parameter cubic EoS, (m^3l)
d	Constant in four-parmater cubic EoS, (m^6/mol^2)
f	Fugacity, (Pa)
G_∞^E	The Gibbs energy at infinite pressure, (J/mol)
H	Molar enthalpy, (J/mol)
$k_1 - k_3$	Constants for EoS alpha-parameter, $(-)$
k_{ij}	Interaction coefficient between component i and j, $(-)$
m_1	Parameter in cubic EoS , $(-)$
m_2	Parameter in cubic EoS , $(-)$
$M_{i,1}$	Composition derivative of m_1 , $(1/mol)$
$M_{i,2}$	Composition derivative of m_2 , $(1/mol)$
N	Total number of moles , (mol)
P	Pressure , (Pa)
R	Universal gas constant , $(J/Kmol)$
S	Molar entropy , $(J/Kmol)$
T	Temperature, (K)
V	Volume , (m^3)
V_m	Molar volume , (m^3/mol)
x	Overall composition, $(-)$
Y	Molar Helmholtz energy, (J/mol)
Z	Compressibility factor, $(-)$

Greek symbols

α	Temperature dependent parameter in cubic EoS., $(-l)$
μ	Chemical potential, (J/mol)
ϕ	Fugacity coefficient, $(-)$
θ_1	Constant in Eq. 3 , $(-)$
θ_2	Constant in Eq. 3 , $(-)$
θ_3	Constant in Eq. 3 , $(-)$
τ_{ij}	Parameter for the Huron-Vidal mixing rule, $(-)$
γ_1	Parameter in Huron-Vidal derivatives., (m^3/mol)
γ_2	Parameter in Huron-Vidal derivatives., (m^3/mol)
γ_3	Parameter in Huron-Vidal derivatives., (m^3/mol)
γ_4	Parameter in Huron-Vidal derivatives., (m^3/mol)
ω	Acentric factor, $(-)$
$\Omega_{a,i}$	Parameter in cubic EoS, $(-)$
$\Omega_{b,i}$	Parameter in cubic EoS, $(-)$

Sub- and superscripts

c	Critical variable

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j	Component denotation
i	Component denotation
ig	Ideal gas value
r	Reduced variable
res	Resdiual
r	Sum counter
z	Sum counter

Abbreviations

CCS	Carbon Capture and Storage
EOS	Equation of State
PR	Peng Robinson
SRK	Soave-Redlich-Kwong
VLE	Vapor-liquid Equilibrium

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A   Derivatives of the short-functions in the F-function

The reduced residual Helmholtz function F is defined by eq. 155

$$F = F(N,T,V,D,B,C) = -Ng(V,B) - \frac{A(T)}{T}f(V,B,C) \tag{155}$$

where the f and g-function can be expressed as from eq. 156

$$f = \frac{h}{m \cdot R \cdot B} \tag{156}$$

$$g = \ln n - \ln V \tag{157}$$

In the implementation, the following short-functions are used:

$$n1(V,B,C) = V - m1 \cdot B \tag{158}$$

$$n2(V,B,C) = V - m2 \cdot B \tag{159}$$

$$n(V,B) = V - B \tag{160}$$

$$m(B,C) = m1 - m2 \tag{161}$$

$$h(V,B,C) = \ln\left(\frac{n2}{n1}\right) = \ln n2 - \ln n1 \tag{162}$$

$m1$ and $m2$ can be zero, constants or functions of B and/or C as explained earlier and listed in Table 1

The required derivatives of these short-functions are:

The first order derivatives:

$$m1_B = \left(\frac{\partial m1}{\partial B}\right)_C \tag{163}$$

$$m2_B = \left(\frac{\partial m2}{\partial B}\right)_C \tag{164}$$

$$m1_C = \left(\frac{\partial m1}{\partial C}\right)_B \tag{165}$$

$$m2_C = \left(\frac{\partial m2}{\partial C}\right)_B \tag{166}$$

$$m_B = m1_B - m2_B \tag{167}$$

$$m_C = m1_C - m2_C \tag{168}$$

$$n1_V = 1.0 \tag{169}$$

$$n2_V = 1.0 \tag{170}$$

$$n1_B = -m1_B \cdot B - m1 \tag{171}$$

$$n2_B = -m2_B \cdot B - m2 \tag{172}$$

$$n1_C = -m1_C \cdot B \tag{173}$$

$$n2_C = -m2_C \cdot B \tag{174}$$

$$h_V = \frac{1}{n2} - \frac{1}{n1} \tag{175}$$

$$h_B = \frac{n2_B}{n2} - \frac{n2_B}{n1} \tag{176}$$

$$h_C = \frac{n2_C}{n2} - \frac{n2_C}{n1} \tag{177}$$

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The second order derivatives:

$$m1_{BB} = \left(\frac{\partial^2 m1}{\partial B^2}\right) \tag{178}$$

$$m2_{BB} = \left(\frac{\partial^2 m2}{\partial B^2}\right) \tag{179}$$

$$m1_{BC} = \left(\frac{\partial^2 m1}{\partial B \partial C}\right) \tag{180}$$

$$m2_{BC} = \left(\frac{\partial^2 m2}{\partial B \partial C}\right) \tag{181}$$

$$m1_{CC} = \left(\frac{\partial^2 m1}{\partial C^2}\right) \tag{182}$$

$$m2_{CC} = \left(\frac{\partial^2 m2}{\partial C^2}\right) \tag{183}$$

$$m_{BB} = m1_{BB} - m2_{BB} \tag{184}$$

$$m_{BC} = m1_{BC} - m2_{BC} \tag{185}$$

$$m_{CC} = m1_{CC} - m2_{CC} \tag{186}$$

$$n1_{BB} = -m1_{BB} \cdot B - 2 \cdot m1_B \tag{187}$$

$$n2_{BB} = -m2_{BB} \cdot B - 2 \cdot m2_B \tag{188}$$

$$n1_{BC} = -m1_{BC} \cdot B - m1_C \tag{189}$$

$$n2_{BC} = -m2_{BC} \cdot B - m2_C \tag{190}$$

$$n1_{CC} = -m1_{CC} \cdot B \tag{191}$$

$$n2_{CC} = -m2_{CC} \cdot B \tag{192}$$

$$h_{VV} = \frac{1}{n1^2} - \frac{1}{n2^2} \tag{193}$$

$$h_{VB} = \frac{n1_B}{n1^2} - \frac{n2_B}{n2^2} \tag{194}$$

$$h_{VC} = \frac{n1_C}{n1^2} - \frac{n2_C}{n2^2} \tag{195}$$

$$h_{BB} = -\frac{n1_{BB}}{n1} + \frac{n2_{BB}}{n2} - \left(\frac{n2_B}{n2}\right)^2 + \left(\frac{n1_B}{n1}\right)^2 \tag{196}$$

$$h_{BC} = -\frac{n1_{BC}}{n1} + \frac{n2_{BC}}{n2} + \frac{n1_B \cdot n1_C}{n1^2} - \frac{n2_B \cdot n2_C}{n2^2} \tag{197}$$

$$h_{CC} = -\frac{n1_{CC}}{n1} + \frac{n2_{CC}}{n2} - \left(\frac{n2_C}{n2}\right)^2 + \left(\frac{n1_C}{n1}\right)^2 \tag{198}$$

The partial derivatives of $m1$ and $m2$ will be specific for each equation of state. For the 2-parameter equations like SRK or Peng-Robinson they will be zero and so will all the following derivatives. The the Schmidt and Wenzel EOS, $m1$ and $m2$ are only functions of C so consequently, the derivatives of B will be zero. For the Patel-Teja EOS, all these derivatives will be "active".