DWSIM - Process Simulation, Modeling and Optimization
Technical Manual

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DWSIM - Process Simulation, Modeling and Optimization

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1 Introduction

The thermodynamic calculations are the basis of simulation in DWSIM. It is important that a process simulator provides to its users several options for calculations in accordance with their needs, their modeled systems, which can range from water to other, more elaborated cases, such as simulations of processes in the petroleum industry, or in a chemical industry.

Regarding phase equilibria, DWSIM, on its current version (1.7), is able to model the vapor-liquid equilibrium (VLE) and hydrocarbon/water systems which exhibit VLLE behavior, considering that water and hydrocarbon liquid phases are immiscible.

The following sections describe the calculation methods used in DWSIM for the physical and chemical description of the elements of a simulation.

2 Thermodynamic Properties

2.1 Phase Equilibria Calculation

In a mixture which find itself in a vapor-liquid equilibria state (VLE), the component fugacities are the same in all phases, that is [1]:

$$f_i^L = f_i^V \tag{2.1}$$

The fugacity of a component in a mixture depends on temperature, pressure and composition. in order to relate f_i^V with temperature, pressure and molar fraction, we define the fugacity coefficient,

$$\phi_i = \frac{f_i^V}{y_i P}, \tag{2.2}$$

which can be calculated from PVT data, commonly obtained from an equation of state. For a mixture of ideal gases, $\phi_i = 1$.

The fugacity of the i component in the liquid phase is related to the composition of that phase by the activity coefficient γ_i, which by itself is related to x_i and standard-state fugacity f_i^0 by

$$\gamma_i = \frac{f_i^L}{x_i f_i^0}. \tag{2.3}$$

The standard state fugacity f_i^0 is the fugacity of the i component in the system temperature, i.e. mixture, and in an arbitrary pressure and composition. in DWSIM, the standard-state fugacity of each component is considered to be equal to pure liquid i at the system temperature and pressure.

If an Equation of State is used to calculate equilibria, fugacity of the i component in the liquid phase is calculated by

$$\phi_i = \frac{f_i^L}{x_i P}, \tag{2.4}$$

with the fugacity coefficient ϕ_i calculated by the EOS, just like it is for the same component in the vapor phase.

The fugacity coefficient of the i component either in the liquid or in the vapor phase is obtained from the same Equation of State through the following expressions

$$RT \ln \phi_i^L = \int_{V^L}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln Z^L, \tag{2.5}$$

$$RT \ln \phi_i^V = \int_{V^V}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln Z^V, \tag{2.6}$$

where the compressibility factor Z is given by

$$Z^L = \frac{PV^L}{RT} \tag{2.7}$$

$$Z^V = \frac{PV^V}{RT} \tag{2.8}$$

2.1.1 Fugacity Coefficient calculation models

Peng-Robinson Equation of State   The Peng-Robinson equation [2] is an cubic Equation of State (characteristic related to the exponent of the molar volume) which relates temperature, pressure and molar volume of a pure component or a mixture of components at equilibrium. The cubic equations are, in fact, the simplest equations capable of representing the behavior of liquid and vapor phases simultaneously. The Peng-Robinson EOS is written in the following form

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{2.9}$$

where

P pressure

R ideal gas universal constant

v molar volume

b parameter related to hard-sphere volume

a parameter related to intermolecular forces

For pure substances, the a and b parameters are given by:

$$a(T) = [1 + (0,37464 + 1,54226\omega - 0,26992\omega^2)(1 - T_r^{(1/2)})]^2 0,45724(R^2 T_c^2)/P_c \tag{2.10}$$

$$b = 0,07780(RT_c)/P_c \tag{2.11}$$

where

ω acentric factor

T_c critical temperature

P_c critical pressure

T_r reduced temperature, T/Tc

For mixtures, equation 2.9 can be used, replacing a and b by mixture-representative values. a and b mixture values are normally given by the basic mixing rule,

$$a_m = \sum_i \sum_j x_i x_j \sqrt{(a_i a_j)}(1 - k_{ij}) \tag{2.12}$$

$$b_m = \sum_i x_i b_i \tag{2.13}$$

where

$x_{i,j}$ molar fraction of the i or j component in the phase (liquid or vapor)

$a_{i,j}$ i or j component a constant

$b_{i,j}$ i or j component b constant

k_{ij} binary interaction parameter which characterizes the i-j pair

The binary interaction parameters used by DWSIM are loaded from the databank and can be modified in the Property Package configuration window.

The fugacity coefficient obtained with the Peng-Robinson EOS in given by

$$\ln \frac{f_i}{x_i P} = \frac{b_i}{b_m}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{\sum_k x_k a_{ki}}{a_m} - \frac{b_i}{b_m}\right)\ln\left(\frac{Z+2,414B}{Z-0,414B}\right), \quad (2.14)$$

where Z in the phase compressibility factor (liquid or vapor) and can be obtained from the equation 2.9,

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - 2B) = 0, \quad (2.15)$$

$$A = \frac{a_m P}{R^2 T^2} \quad (2.16)$$

$$B = \frac{b_m P}{RT} \quad (2.17)$$

$$Z = \frac{PV}{RT} \quad (2.18)$$

Soave-Redlich-Kwong Equation of State   The Soave-Redlich-Kwong Equation [3] is also a cubic equation of state in volume,

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)}, \quad (2.19)$$

The a and b parameters are given by:

$$a(T) = [1 + (0,48 + 1,574\omega - 0,176\omega^2)(1 - T_r^{(1/2)})]^2 0,42747(R^2 T_c^2)/P_c \quad (2.20)$$

$$b = 0,08664(RT_c)/P_c \quad (2.21)$$

The equations 2.12 and 2.13 are used to calculate mixture parameters. Fugacity is calculated by

$$\ln \frac{f_i}{x_i P} = \frac{b_i}{b_m}(Z-1) - \ln(Z-B) - \frac{A}{B}\left(\frac{\sum_k x_k a_{ki}}{a_m} - \frac{b_i}{b_m}\right)\ln\left(\frac{Z+B}{Z}\right) \quad (2.22)$$

The phase compressibility factor Z is obtained from the equation 2.19,

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0, \quad (2.23)$$

$$A = \frac{a_m P}{R^2 T^2} \quad (2.24)$$

$$B = \frac{b_m P}{RT} \tag{2.25}$$

$$Z = \frac{PV}{RT} \tag{2.26}$$

The equations 2.15 and 2.23, in low temperature and pressure conditions, can provide three roots for Z. In this case, if liquid properties are being calculated, the smallest root is used. If the phase is vapor, the largest root is used. The remaining root has no physical meaning; at high temperatures and pressures (conditions above the pseudocritical point), the equations 2.15 and 2.23 provides only one real root.

Peng-Robinson with Volume Translation   Volume translation solves the main problem with two-constant EOS's, poor liquid volumetric predictions. A simple correction term is applied to the EOS-calculated molar volume,

$$v = v^{EOS} - c, \tag{2.27}$$

where $v =$corrected molar volume, $v^{EOS} =$EOS-calculated volume, and $c =$component-specific constant. The shift in volume is actually equivalent to adding a third constant to the EOS but is special because equilibrium conditions are unaltered.

It is also shown that multicomponent VLE is unaltered by introducing the volume-shift term c as a mole-fraction average,

$$v_L = v_L^{EOS} - \sum x_i c_i \tag{2.28}$$

Volume translation can be applied to any two-constant cubic equation, thereby eliminating the volumetric defficiency suffered by all two-constant equations [4].

2.1.2 Chao-Seader and Grayson-Streed models

Chao-Seader ([5]) and Grayson-Streed ([6]) are older, semi-empirical models. The Grayson-Streed correlation is an extension of the Chao-Seader method with special applicability to hydrogen. In DWSIM, only the equilibrium values produced by these correlations are used in the calculations. The Lee-Kesler method is used to determine the enthalpy and entropy of liquid and vapor phases.

Chao Seader   Use this method for heavy hydrocarbons, where the pressure is less than 10 342 kPa (1 500 psia) and the temperature is between the range -17.78 žC and 260 žC.

Grayson Streed   Recommended for simulating heavy hydrocarbon systems with a high hydrogen content.

2.1.3 Calculation models for the liquid phase activity coefficient

The activity coefficient (γ) is a factor used in thermodynamics to account for deviations from ideal behaviour in a mixture of chemical substances. In an ideal mixture, the interactions between each pair of chemical species are the same (or more formally, the enthalpy of mixing is zero) and,

as a result, properties of the mixtures can be expressed directly in terms of simple concentrations or partial pressures of the substances present. Deviations from ideality are accommodated by modifying the concentration by an activity coefficient. . The activity coefficient is defined as

$$\gamma_i = [\frac{\partial(nG^E/RT)}{\partial n_i}]_{P,T,n_{j\neq i}} \tag{2.29}$$

where G^E represents the excess Gibbs energy of the liquid solution, which is a measure of how far the solution is from ideal behavior. For an ideal solution, $\gamma_i = 1$. Expressions for G^E/RT provide values for the activity coefficients.

UNIQUAC and UNIFAC models   The UNIQUAC equation considers $g \equiv G^E/RT$ formed by two additive parts, one combinatorial term g^C to take into account the size of the molecules, and one residual term g^R, which take into account the interactions between molecules:

$$g \equiv g^C + g^R \tag{2.30}$$

The g^C function contains only pure species parameters, while the g^R function incorporates two binary parameters for each pair of molecules. For a multicomponent system,

$$g^C = \sum_i x_i \ln \phi_i/x_i + 5 \sum_i q_i x_i \ln \theta_i/\phi_i \tag{2.31}$$

and

$$g^R = -\sum_i q_i x_i \ln(\sum_j \theta_j \tau_j i) \tag{2.32}$$

where

$$\phi_i \equiv (x_i r_i)/(\sum_j x_j r_j) \tag{2.33}$$

and

$$\theta_i \equiv (x_i q_i)/(\sum_j x_j q_j) \tag{2.34}$$

The i subscript indicates the species, and j is an index that represents all the species, i included. All sums are over all the species. Note that $\tau_{ij} \neq \tau_{ji}$. When $i = j$, $\tau_{ii} = \tau_{jj} = 1$. In these equations, r_i (a relative molecular volume) and q_i (a relative molecular surface area) are pure species parameters. The influence of temperature in g enters by means of the τ_{ij} parameters, which are temperature-dependent:

$$\tau_{ij} = \exp(u_{ij} - u_{jj})/RT \tag{2.35}$$

This way, the UNIQUAC parameters are values of $(u_{ij} - u_{jj})$.

An expression for γ_i is found through the application of the following relation:

$$\ln \gamma_i = \left[\partial(nG^E/RT)/\partial n_i\right]_{(P,T,n_{j\neq i})} \tag{2.36}$$

The result is represented by the following equations:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{2.37}$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5 q_i (1 - J_i/L_i + \ln J_i/L_i) \tag{2.38}$$

$$\ln \gamma_i^R = q_i (1 - \ln s_i - \sum_j \theta_j \tau_{ij}/s_j) \tag{2.39}$$

where

$$J_i = r_i / (\sum_j r_j x_j) \tag{2.40}$$

$$L = q_i / (\sum_j q_j x_j) \tag{2.41}$$

$$s_i = \sum_l \theta_l \tau_{li} \tag{2.42}$$

Again the i subscript identify the species, j and l are indexes which represent all the species, including i. all sums are over all the species, and $\tau_{ij} = 1$ for $i = j$. The parameters values $(u_{ij} - u_{jj})$ are found by regression of binary VLE data.

The UNIFAC method for the estimation of activity coefficients depends on the concept of that a liquid mixture can be considered a solution of its own molecules. These structural units are called subgroups. The greatest advantage of this method is that a relatively small number of subgroups can be combined to form a very large number of molecules.

The activity coefficients do not only depend on the subgroup properties, but also on the interactions between these groups. Similar subgroups are related to a main group, like "CH2", "OH", "ACH" etc.; the identification of the main groups are only descriptive. All the subgroups that belongs to the same main group are considered identical with respect to the interaction between groups. Consequently, the parameters which characterize the interactions between the groups are identified by pairs of the main groups.

The UNIFAC method is based on the UNIQUAC equation, where the activity coefficients are given by the equation 2.36. When applied to a solution of groups, the equations 2.38 and 2.39 are written in the form:

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5 q_i (1 - J_i/L_i + \ln J_i/L_i) \tag{2.43}$$

$$\ln \gamma_i^R = q_i (1 - \sum_k (\theta_k \beta_{ik}/s_k) - e_{ki} ln \beta_{ik}/s_k) \tag{2.44}$$

The parameters J_i e L_i are still given by eqs. 2.54 and **??**. Furthermore, the following definitions apply:

$$r_i = \sum_k v_k^{(i)} R_k \tag{2.45}$$

$$q_i = \sum_k v_k^{(i)} Q_k \tag{2.46}$$

$$e_{ki} = (\nu_k^{(i)} Q_k)/q_i \tag{2.47}$$

$$\beta_{ik} = \sum_m e_{mk}\tau_{mk} \tag{2.48}$$

$$\theta_k = (\sum_i x_i q_i e_{ki})/(\sum_i x_j q_j) \tag{2.49}$$

$$s_k = \sum_m \theta_m \tau_{mk} \tag{2.50}$$

$$s_i = \sum_l \theta_l \tau_{li} \tag{2.51}$$

$$\tau_{mk} = \exp(-a_{mk})/T \tag{2.52}$$

The i subscript identify the species, and j is an index that goes through all the species. The k subscript identify the subgroups, and m is an index that goes through all the subgroups. The parameter $\nu_k^{(i)}$ is the number of the k subgroup in a molecule of the i species. The subgroup parameter values R_k and Q_k and the interaction parameters $-a_{mk}$ are obtained in the literature.

Modified UNIFAC (Dortmund) model The UNIFAC model, despite being widely used in various applications, has some limitations which are, in some way, inherent to the model. Some of these limitations are:

1. UNIFAC is unable to distinguish between some types of isomers.

2. The $\gamma - \phi$ approach limits the use of UNIFAC for applications under the pressure range of 10-15 atm.

3. The temperature is limited within the range of approximately 275-425 K.

4. Non-condensable gases and supercritical components are not included.

5. Proximity effects are not taken into account.

6. The parameters of liquid-liquid equilibrium are different from those of vapor-liquid equilibrium.

7. Polymers are not included.

8. Electrolytes are not included.

Some of these limitations can be overcome. The insensitivity of some types of isomers can be eliminated through a careful choice of the groups used to represent the molecules. The fact that the parameters for the liquid-liquid equilibrium are different from those for the vapor-liquid equilibrium seems not to have a theoretical solution at this time. One solution is to use both data from both equiibria to determine the parameters as a modified UNIFAC model. The limitations on the pressure and temperature can be overcome if the UNIFAC model is used with equations of state, which carry with them the dependencies of pressure and temperature.

These limitations of the original UNIFAC model have led several authors to propose changes in both combinatorial and the residual parts. To modify the combinatorial part, the basis is the suggestion given by Kikic et al. (1980) in the sense that the Staverman-Guggenheim correction on the original term of Flory-Huggins is very small and can, in most cases, be neglected. As a result, this correction was empirically removed from the UNIFAC model. Among these modifications, the proposed by Gmehling and coworkers [Weidlich and Gmehling, 1986; Weidlich and Gmehling, 1987; Gmehling et al., 1993], known as the model UNIFAC-Dortmund, is one of the most promising. In this model, the combinatorial part of the original UNIFAC is replaced by:

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i(1 - J_i/L_i + \ln J_i/L_i) \qquad (2.53)$$

$$J_i = r_i^{3/4}/(\sum_j r_j^{3/4} x_j) \qquad (2.54)$$

where the remaining quantities is defined the same way as in the original UNIFAC. Thus, the correction in-Staverman Guggenheim is empirically taken from the template. It is important to note that the in the UNIFAC-Dortmund model, the quantities R_k and Q_k are no longer calculated on the volume and surface area of Van der Waals forces, as proposed by Bondi (1968), but are additional adjustable parameters of the model.

The residual part is still given by the solution for groups, just as in the original UNIFAC, but now the parameters of group interaction are considered temperature dependent, according to:

$$\tau_{mk} = \exp(-a_{mk}^{(0)} + a_{mk}^{(1)}T + a_{mk}^{(2)}T^2)/T \qquad (2.55)$$

These parameters must be estimated from experimental phase equilibrium data. Gmehling et al. (1993) presented an array of parameters for 45 major groups, adjusted using data from the vapor-liquid equilibrium, excess enthalpies, activity coefficients at infinite dilution and liquid-liquid equilibrium. enthalpy and entropy of liquid and vapor.

NRTL model   Wilson (1964) presented a model relating g^E to the molar fraction, based mainly on molecular considerations, using the concept of local composition. Basically, the concept of local composition states that the composition of the system in the vicinity of a given molecule is not equal to the overall composition of the system, because of intermolecular forces.

Wilson's equation provides a good representation of the Gibbs' excess free energy for a variety of mixtures, and is particularly useful in solutions of polar compounds or with a tendency to association in apolar solvents, where Van Laar's equation or Margules' one are not sufficient. Wilson's equation has the advantage of being easily extended to multicomponent solutions but has two disadvantages: first, the less important, is that the equations are not applicable to systems where the logarithms of activity coefficients, when plotted as a function of *x*, show a maximum or a minimum. However, these systems are not common. The second, a little more serious, is that the model of Wilson is not able to predict limited miscibility, that is, it is not useful for LLE calculations.

Renon and Prausnitz [7] developed the *NRTL* equation *(Non-Random, Two-Liquid)* based on the concept of local composition but, unlike Wilson's model, the NRTL model is applicable to systems of partial miscibility. The model equation is:

$$\ln \gamma_i = \frac{\sum\limits_{j=1}^{n} \tau_{ji} x_j G_{ji}}{\sum\limits_{k=1}^{n} x_k G_{ki}} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum\limits_{k=1}^{n} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum\limits_{m=1}^{n} \tau_{mj} x_m G_{mj}}{\sum\limits_{k=1}^{n} x_k G_{kj}} \right), \qquad (2.56)$$

$$G_{ij} = exp(-\tau_{ij}\alpha_{ij}), \qquad (2.57)$$

$$\tau_{ij} = a_{ij}/RT, \qquad (2.58)$$

where

γ_i Activity coefficient of component *i*

x_i Molar fraction of component *i*

a_{ij} Interaction parameter between *i-j* ($a_{ij} \neq a_{ji}$) (cal/mol)

T Temperature (K)

α_{ij} non-randomness parameter for the *i-j* pair ($\alpha_{ij} = \alpha_{ji}$)

The significance of G_{ij} is similar to Λ_{ij} from Wilson's equation, that is, they are characteristic energy parameters of the *ij* interaction. The parameter is related to the non-randomness of the mixture, i.e. that the components in the mixture are not randomly distributed but follow a pattern dictated by the local composition. When it is zero, the mixture is completely random, and the equation is reduced to the two-suffix Margules equation.

For ideal or moderately ideal systems, the NRTL model does not offer much advantage over Van Laar and three-suffix Margules, but for strongly non-ideal systems, this equation can provide a good representation of experimental data, although good quality data is necessary to estimate the three required parameters.

2.2 Enthalpy, Entropy and Heat Capacities

H^{id} values are calculated from the ideal gas heat capacity. For mixtures, a molar average is used. The value calculated by the EOS is for the phase, independently of the number of components present in the mixture.

Peng-Robinson, Soave-Redlich-Kwong   For the cubic equations of state, enthalpy, entropy and heat capacities are calculated by the *departure functions*, which relates the phase properties in the conditions of the mixture with the same mixture property in the ideal gas state. This way, the following departure functions are defined [8],

$$\frac{H - H^{id}}{RT} = X; \frac{S - S^{id}}{R} = Y \qquad (2.59)$$

values for X and Y are calculated by the PR and SRK EOS, according to the table 1:

In DWSIM, $P_o = 1$ atm.

Heat capacities are obtained directly from the EOS, by using the following thermodynamic relations:

$$C_p - C_p^{id} = T \int\limits_{\infty}^{V} \left(\frac{\partial^2 P}{\partial T^2} \right) dV - \frac{T(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} - R \qquad (2.60)$$

Table 1: Enthalpy/Entropy calculation with an EOS

	$\frac{H-H^{id}}{RT}$	$\frac{S-S^{id}}{R}$
PR	$Z - 1 - \frac{1}{2^{1,5}bRT}\left[a - T\frac{da}{dT}\right] \times$	$\ln(Z-B) - \ln\frac{P}{P^0} - \frac{A}{2^{1,5}bRT}\left[\frac{T}{a}\frac{da}{dT}\right] \times$
	$\times \ln\left[\frac{V+2,414b}{V+0,414b}\right]$	$\times \ln\left[\frac{V+2,414b}{V+0,414b}\right]$
SRK	$Z - 1 - \frac{1}{bRT}\left[a - T\frac{da}{dT}\right] \times$	$\ln(Z-B) - \ln\frac{P}{P^0} - \frac{A}{B}\left[\frac{T}{a}\frac{da}{dT}\right] \times$
	$\times \ln\left[1 + \frac{b}{V}\right]$	$\times \ln\left[1 + \frac{B}{Z}\right]$

$$C_p - C_v = -T\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{2.61}$$

Lee-Kesler   Enthalpies, entropies and heat capacities are calculated by the Lee-Kesler model [9] through the following equations:

$$\frac{H - H^{id}}{RT_c} = T_r\left(Z - 1 - \frac{b_2 + 2b_3/T_r + 3b_4/T_r^2}{T_r V_r} - \frac{c_2 - 3c_3/T_r^2}{2T_r V_r^2} + \frac{d_2}{5T_r V_r^2} + 3E\right) \tag{2.62}$$

$$\frac{S - S^{id}}{R} + \ln\left(\frac{P}{P_0}\right) = \ln Z - \frac{b_2 + b_3/T_r^2 + 2b_4/T_r^3}{V_r} - \frac{c_1 - 2c_3/T_r^3}{2V_r^2} + \frac{d_1}{5V_r^5} + 2E \tag{2.63}$$

$$\frac{C_v - C_v^{id}}{R} = \frac{2\left(b_3 + 3b_4/T_r\right)}{T_r^2 V_r} - \frac{3c_3}{T_r^3 V_r^2} - 6E \tag{2.64}$$

$$\frac{C_p - C_p^{id}}{R} = \frac{C_v - C_v^{id}}{R} - 1 - T_r\frac{\left(\frac{\partial P_r}{\partial T_r}\right)_{V_r}^2}{\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r}} \tag{2.65}$$

$$E = \frac{c_4}{2T_r^3 \gamma}\left[\beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)\right] \tag{2.66}$$

It is necessary an iterative method to calculate V_r. This way, the user should always watch the values generated by DWSIM in order to detect any incoherence in the compressibility factors generated by the Lee-Kesler model.

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right) \tag{2.67}$$

$$B = b_1 - b_2/T_r - b_3/T_r^2 - b_4/T_r^3 \tag{2.68}$$

$$C = c_1 - c_2/T_r + c_3/T_r^3 \tag{2.69}$$

$$D = d_1 + d_2/T_r \tag{2.70}$$

Each property must be calculated based in two fluids apart from the main one, one simple and other for reference. For example, for the compressibility factor,

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}} \left(Z^{(r)} - Z^{(0)} \right), \tag{2.71}$$

where the (0) superscript refers to the simple fluid while the (r) superscript refers to the reference fluid. This way, property calculation by the Lee-Kesler model should follow the sequence below (enthalpy calculation example):

1. V_r and $Z^{(0)}$ are calculated for the simple fluid at the fluid T_r and P_r. using the equation 2.62, and with the constants for the simple fluid, as shown in the table 3, $(H - H^0)/RT_c$ is calculated. This term is $\left[(H - H^0)/RT_c \right]^{(0)}$. in this calculation, Z in the equation 2.62 is $Z^{(0)}$.

2. The step 1 is repeated, using the same T_r and P_r, but using the constants for the reference fluid as shown in table 3. With these values, the equation 2.62 allows the calculation of $\left[(H - H^0)/RT_c \right]^{(r)}$. In this step, Z in the equation 2.62 is $Z^{(r)}$.

3. Finally, one determines the residual enthalpy for the fluid of interest by

$$
\begin{aligned}
\left[(H - H^0)/RT_c \right] &= \left[(H - H^0)/RT_c \right]^{(0)} + \\
&\quad \frac{\omega}{\omega^{(r)}} \left(\left[(H - H^0)/RT_c \right]^{(r)} - \left[(H - H^0)/RT_c \right]^{(0)} \right), \quad (2.72)
\end{aligned}
$$

where $\omega^{(r)} = 0,3978$.

Table 3: Constants for the Lee-Kesler model

Constant	Simple Fluid	Reference Fluid
b_1	0,1181193	0,2026579
b_2	0,265728	0,331511
b_3	0,154790	0,027655
b_4	0,030323	0,203488
c_1	0,0236744	0,0313385
c_2	0,0186984	0,0503618
c_3	0,0	0,016901
c_4	0,042724	0,041577
$d_1 \times 10^4$	0,155488	0,48736
$d_2 \times 10^4$	0,623689	0,0740336
β	0,65392	1,226
γ	0,060167	0,03754

3 Transport Properties

3.1 Density

Liquid Phase   Liquid phase density is calculated with the Rackett equation [8],

$$V_s = \frac{RT_C}{P_C} Z_{RA}^{\left[1+(1-T_r)^{2/7}\right]},$$

(3.1)

where:

V_s Saturated molar volume (m³/mol)

T_c Critical temperature (K)

P_c Critical pressure (Pa)

T_r Reduced temperature

Z_{RA} Rackett constant of the component (or the mixture)

R Ideal Gas constant (8,314 J/[mol.K])

If $T \geqslant T_{cm}$, the Rackett method does not provide a value for V_s and, in this case, DWSIM uses the EOS-generated compressibility factor to calculate the density of the liquid phase.

For mixtures, the equation 3.1 becomes

$$V_s = R \left(\sum \frac{x_i T_{c_i}}{P_{c_i}} \right) Z_{RA}^{\left[1+(1-T_r)^{2/7}\right]},$$

(3.2)

with $T_r = T/T_{cm}$, and

$$T_{c_m} = \sum \sum \phi_i \phi_j T_{c_{ij}},$$

(3.3)

$$\phi_i = \frac{x_i V_{c_i}}{\sum x_i V_{c_i}},$$

(3.4)

$$T_{c_{ij}} = \left[\frac{8 \left(V_{c_i} V_{c_j} \right)^{1/2}}{\left(V_{c_i}^{1/3} + V_{c_j}^{1/3} \right)^3} \right] \left(T_{c_i} T_{c_j} \right)^{1/2},$$

(3.5)

where:

x_i Molar fraction

V_{c_i} Critical volume (m³/mol)

If Z_{RA} isn't available, it is calculated from the component acentric factor,

$$Z_{RA} = 0,2956 - 0,08775\omega,$$

(3.6)

If the component (or mixture) isn't saturated, a correction is applied in order to account for the effect of pressure in the volume,

$$V = V_s \left[1 - (0,0861488 + 0,0344483\omega) \ln \frac{\beta + P}{\beta + P_{vp}} \right],$$

(3.7)

---

with

$$\frac{\beta}{P} = -1 - 9,070217\,(1 - T_r)^{1/3} + 62,45326\,(1 - T_r)^{2/3} - 135,1102\,(1 - T_r) +$$
$$+ \exp\left(4,79594 + 0,250047\omega + 1,14188\omega^2\right)(1 - T_r)^{4/3}, \tag{3.8}$$

where:

V Compressed liquid volume (m³/mol)

P Pressure (Pa)

P_{vp} Vapor pressure / Bubble point pressure (Pa)

Finally, density is calculated from the molar volume by the following relation:

$$\rho = \frac{MM}{1000V}, \tag{3.9}$$

where:

ρ Density (kg/m³)

V Specific volume of the fluid (m³/mol)

MM Liquid phase molecular volume (kg/kmol)

For the Ideal Gas *Property Package, the compressibility factor is considered to be equal to 1.*

Vapor Phase   Vapor phase density is calculated from the compressiblity factor generated by the EOS, according with the following equation:

$$\rho = \frac{MM\,P}{1000ZRT}, \tag{3.10}$$

where:

ρ Density (kg/m³)

MM Molecular weight of the vapor phase (kg/kmol)

P Pressure (Pa)

Z Vapor phase compressibility factor

R Ideal Gas constant (8,314 J/[mol.K])

T Temperature (K)

Mixture   If there are two phases at system temperature and pressure, the density of the mixture is calculated by the following expression:

$$\rho_m = f_l\rho_l + f_v\rho_v, \tag{3.11}$$

where:

$\rho_{m,l,v}$ Density of the mixture / liquid phase / vapor phase (kg/m³)

$f_{l,v}$ Volumetric fraction of the liquid phase / vapor phase (kg/kmol)

3.2 Viscosity

Liquid Phase   Liquid phase viscosity is calculated from

$$\eta_L = \exp\left(\sum_i x_i \ln \eta_i\right),\tag{3.12}$$

where η_i is the viscosity of each component in the phase, which depends on the temperature and is calculated from experimental data. Dependence of viscosity with the temperature is described in the equation

$$\eta = \exp\left(A + B/T + C\ln T + DT^E\right),\tag{3.13}$$

where A, B, C, D and E are experimental coefficients (or generated by DWSIM in the case of pseudocomponents or hypotheticals).

Vapor Phase   Vapor phase viscosity is calculated in two steps. First, the temperature dependence is given by the *Lucas* equation [8],

$$\eta\xi = \left[0,807T_r^{0,618} - 0,357\exp(-0,449T_r) + 0,34\exp(-4,058T_r) + 0,018\right]\tag{3.14}$$

$$\xi = 0,176\left(\frac{T_c}{MM^3P_c^4}\right)^{1/6},\tag{3.15}$$

where

η	Viscosity (μP)
T_c, P_c	Component (or mixture) critical properties
T_r	Reduced temperature, T/T_c
MM	Molecular weight (kg/kmol)

In the second step, the calculated viscosity with the Lucas method is corrected to take into account the effect of pressure, by the *Jossi-Stiel-Thodos* method [8],

$$\left[(\eta - \eta_0)\left(\frac{T_c}{MM^3P_c^4}\right)^{1/6} + 1\right]^{1/4} = 1,023 + 0,23364\rho_r +$$
$$+\ 0,58533\rho_r^2 - 0,40758\rho_r^3 + 0,093324\rho_r^4,\tag{3.16}$$

where

η, η_0	Corrected viscosity / Lucas method calculated viscosity (μP)
T_c, P_c	Component critical properties
ρ_r	Reduced density, $\rho/\rho_c = V/V_c$
MM	Molecular weight (kg/kmol)

If the vapor phase contains more than a component, the viscosity is calculated by the same procedure, but with the required properties calculated by a molar average.

3.3 Surface Tension

The liquid phase surface tension is calculated by doing a molar average of the individual component tensions, which are calculated with the *Brock-Bird* equation [8],

$$\frac{\sigma}{P_c^{2/3} T_c^{1/3}} = (0,132\alpha_c - 0,279)(1-T_r)^{11/9} \tag{3.17}$$

$$\alpha_c = 0,9076 \left[1 + \frac{T_{br} \ln(P_c/1,01325)}{1 - T_{br}} \right], \tag{3.18}$$

where

σ Surface tension (N/m)

T_c Critical temperature (K)

P_c Critical pressure (Pa)

T_{br} Reduced normal boiling point, T_b/T_c

4 Thermal Properties

4.1 Thermal Conductivity

Liquid Phase   The contribution of each component for the thermal conductivity of the liquid phase is calculated by the *Latini* method [8],

$$\lambda_i \quad = \quad \frac{A(1 - T_r)^{0,38}}{T_r^{1/6}} \tag{4.1}$$

$$A \quad = \quad \frac{A^* T_b^{0,38}}{MM^\beta T_c^\gamma}, \tag{4.2}$$

where A^*, α, β and γ depend on the nature of the liquid (Saturated Hydrocarbon, Aromatic, Water, etc). The liquid phase thermal conductivity is calculated from the individual values by the *Li* method [8],

$$\lambda_L \quad = \sum\sum \phi_i \phi_j \lambda_{ij} \tag{4.3}$$

$$\lambda_{ij} \quad = \quad 2(\lambda_i^{-1} + \lambda_j^{-1})^{-1} \tag{4.4}$$

$$\phi_i = \frac{x_i V_{c_i}}{\sum x_i V_{c_i}}, \tag{4.5}$$

where

λ_L liquid phase thermal conductivity (W/[m.K])

Vapor Phase   Vapor phase thermal conductivity is calculated by the *Ely and Hanley* method [8],

$$\lambda_V = \lambda^* + \frac{1000\eta^*}{MM} 1,32 \left(C_v - \frac{3R}{2} \right), \tag{4.6}$$

where

λ_V vapor phase thermal conductivity (W/[m.K])

C_v constant volume heat capacity (J/[mol.K])

λ^*e η^* are defined by:

$$\lambda^* = \lambda_0 H \tag{4.7}$$

$$H = \left(\frac{16,04.10^{-3}}{MM/1000} \right)^{1/2} f^{1/2} / h^{2/3} \tag{4.8}$$

$$\lambda_0 = 1944\eta_0 \tag{4.9}$$

$$f = \frac{T_0\theta}{190,4} \tag{4.10}$$

$$h = \frac{V_c}{99,2}\phi \tag{4.11}$$

$$\theta = 1 + (\omega - 0,011)(0,56553 - 0,86276\ln T^+ - 0,69852/T^+) \tag{4.12}$$

$$\phi = \left[1 + (\omega - 0,011)(0,38650 - 1,1617\ln T^+)\right]0,288/Z_c \tag{4.13}$$

If $T_r \leqslant 2$, $T^+ = T_r$. If $T_r > 2$, $T^+ = 2$.

$$h = \frac{V_c}{99,2}\phi \tag{4.14}$$

$$\eta^* = \eta_0 H \frac{MM/1000}{16,04.10^{-3}} \tag{4.15}$$

$$\eta_0 = 10^{-7}\sum_{n=1}^{9} C_n T_0^{(n-4)/3} \tag{4.16}$$

$$T_0 = T/f \tag{4.17}$$

5 Reactions

DWSIM includes support for chemical reactions through the Chemical Reactions Manager. Three types of reactions are available to the user:

Conversion, where you must specify the conversion (%) of the limiting reagent as a function of temperature

Equilibrium, where you must specify the equilibrium constant (K) as a function of temperature, a constant value or calculated from the Gibbs free energy of reaction ($\Delta G / R$). The orders of reaction of the components are obtained from the stoichiometric coefficients.

Kinetic, where you should specify the frequency factor (A) and activation energy (E) for the direct reaction (optionally for the reverse reaction), including the orders of reaction (direct and inverse) of each component.

For each chemical reaction is necessary to specify the stoichiometric coefficients of the components and a component-base - required a reagent, used as reference for calculating the heat of reaction. The sequential reactions DWSIM both as parallel (this behavior is defined in the editor, sets of reactions).

5.1 Conversion Reaction

In the conversion reaction it is assumed that the user has information regarding the conversion of one of the reactants as a function of temperature. By knowing the conversion and the stoichiometric coefficients, the quantities of the other components in the reaction can be calculated.

Considering the following chemical reaction:

$$aA + bB \rightarrow cC, \tag{5.1}$$

where a, b and c are the stoichiometric coefficients of reactants and product, respectively. A is the limiting reactant and B is in excess. The amount of each component at the end of the reaction can then be calculated from the following stoichiometric relationships:

$$N_A = N_{A_0} - N_{A_0} X_A \tag{5.2}$$

$$N_B = N_{B_0} - \frac{b}{a} N_{A_0} X_A \tag{5.3}$$

$$N_C = N_{C_0} + \frac{c}{a} (N_{A_0} X_A) \tag{5.4}$$

where $N_{A,B,C}$ are the molar amounts of the components at the end of the reaction, N_{A_0,B_0,C_0} are the molar amount of the components at the start of the reaction and X_A is the conversion of the base-reactant A.

5.2 Equilibrium Reaction

In the equilibrium reaction, the quantity of each component at the equilibrium is related to equilibrium constant by the following relationship:

$$K = \prod_{j=1}^{n}(q_j)^{\nu_j}, \tag{5.5}$$

where K is the equilibrium constant, q is the basis of components (partial pressure in the vapor phase or activity in the liquid phase) ν is the stoichiometric coefficient of component j and n is the number of components in the reaction.

The equilibrium constant can be obtained by three different means. One is to consider it a constant, another is considering it as a function of temperature, and finally calculate it automatically from the Gibbs free energy at the temperature of the reaction. The first two methods require user input.

5.2.1 Solution method

For each reaction that is occurring in parallel in the system, we can define ξ as the *reaction extent*, so that the molar amount of each component in the equilibrium is obtained by the following relationship:

$$N_j = N_{j_0} + \sum_i \nu_{ij}\xi_i, \tag{5.6}$$

where ξ_i is the coordinate of the reaction i and ν_{ij} is the stoichiometric coefficient of the j component at reaction i. Defining the molar fraction of the component i as $x_j = n_j/n_t$, where n_t is the total number of mols, including inerts, whe have the following expression for each reaction i:

$$f_i(\xi) = \sum_i \ln(x_i) - \ln(K_i) = 0, \tag{5.7}$$

where the system of equations F can be easily solved by Newton-Raphson's method [10].

5.3 Kinetic Reaction

The kinetic reaction is defined by the parameters of the equation of Arrhenius (frequency factor and activation energy) for both the direct order and for the reverse order. Suppose we have the following kinetic reaction:

$$aA + bB \rightarrow cC + dD \tag{5.8}$$

The reaction rate for the A component can be defined as

$$r_A = k[A][B] - k'[C][D] \tag{5.9}$$

where

$$k = A \exp\left(-E/RT\right) \qquad (5.10)$$

$$k' = A' \exp\left(-E'/RT\right) \qquad (5.11)$$

The kinetic reactions are used in Plug-Flow Reactors (PFRs) and in Continuous-Stirred Tank Reactors (CSTRs). In them, the relationship between molar concentration and the rate of reaction is given by

$$F_A = F_{A_0} + \int^V r_A dV, \qquad (5.12)$$

where F_A is the molar flow of the A component and V is the reactor volume.

6 Property Estimation Methods

6.1 Petroleum Fractions

6.1.1 Molecular weight

Riazi and Al Sahhaf method [11]

$$MM = \left[\frac{1}{0,01964}(6,97996 - \ln(1080 - T_b))\right]^{3/2}, \qquad (6.1)$$

where

MM Molecular weight (kg/kmol)

T_b Boiling point at 1 atm (K)

If the specific gravity (SG) is available, the molecular weight is calculated by

$$\begin{aligned} MM =\ & 42,965[\exp(2,097 \times 10^{-4}T_b - 7,78712SG + \\ & +2,08476 \times 10^{-3}T_bSG)]T_b^{1,26007}SG^{4,98308} \end{aligned} \qquad (6.2)$$

Winn [12]

$$MM = 0,00005805PEMe^{2,3776}/d15^{0,9371}, \qquad (6.3)$$

where

$PEMe$ Mean Boiling Point (K)

$d15$ Specific Gravity @ 60 °F

Riazi[12]

$$
\begin{aligned}
MM \quad = \quad & 42,965\exp(0,0002097PEMe - 7,78d15 + 0,00208476 \times PEMe \times d15) \times \\
& \times PEMe^{1,26007}d15^{4,98308} \qquad\qquad\qquad\qquad\qquad\qquad\qquad (6.4)
\end{aligned}
$$

Lee-Kesler[12]

$$
\begin{aligned}
t_1 \quad = \quad & -12272,6 + 9486,4d15 + (8,3741 - 5,9917d15)PEMe & (6.5) \\
t_2 \quad = \quad & (1 - 0,77084d15 - 0,02058d15^2) \times \\
& \times (0,7465 - 222,466/PEMe) \times 10^7/PEMe & (6.6) \\
t_3 \quad = \quad & (1 - 0,80882d15 - 0,02226d15^2) \times \\
& \times (0,3228 - 17,335/PEMe) \times 10^{12}/PEMe^3 & (6.7) \\
MM \quad = \quad & t_1 + t_2 + t_3 & (6.8)
\end{aligned}
$$

Farah

$$
\begin{aligned}
MM \quad = \quad & \exp(6,8117 + 1,3372A - 3,6283B) & (6.9) \\
MM \quad = \quad & \exp(4,0397 + 0,1362A - 0,3406B - 0,9988d15 + 0,0039PEMe), & (6.10)
\end{aligned}
$$

where

A, B *Walther-ASTM* equation parameters for viscosity calculation

6.1.2 Specific Gravity

Riazi e Al Sahhaf [11]

$$
SG = 1,07 - \exp(3,56073 - 2,93886MM^{0,1}), \qquad\qquad (6.11)
$$

where

SG Specific Gravity

MM Molecular weight (kg/kmol)

6.1.3 Critical Properties

Lee-Kesler [11]

$$
T_c = 189,8 + 450,6SG + (0,4244 + 0,1174SG)T_b + (0,1441 - 1,0069SG)10^5/T_b \quad (6.12)
$$

$$
\begin{aligned}
\ln P_c \quad = \quad & 5,689 - 0,0566/SG - (0,43639 + 4,1216/SG + 0,21343/SG^2) \times \\
& \times 10^{-3}T_b + (0,47579 + 1,182/SG + 0,15302/SG^2) \times 10^{-6} \times T_b^2 - \\
& -(2,4505 + 9,9099/SG^2) \times 10^{-10} \times T_b^3, & (6.13)
\end{aligned}
$$

where

T_b NBP (K)

T_c Critical temperature (K)

P_c Critical pressure (bar)

Farah

$$
\begin{align}
T_c &= 731,968 + 291,952A - 704,998B \tag{6.14} \\
T_c &= 104,0061 + 38,75A - 41,6097B + 0,7831PEMe \tag{6.15} \\
T_c &= 196,793 + 90,205A - 221,051B + 309,534d15 + 0,524PEMe \tag{6.16}
\end{align}
$$

$$
\begin{align}
P_c &= \exp(20,0056 - 9,8758\ln(A) + 12,2326\ln(B)) \tag{6.17} \\
P_c &= \exp(11,2037 - 0,5484A + 1,9242B + 510,1272/PEMe) \tag{6.18} \\
P_c &= \exp(28,7605 + 0,7158\ln(A) - 0,2796\ln(B) + 2,3129\ln(d15) - 2,4027\ln(PEMe)) \tag{6.19}
\end{align}
$$

Riazi-Daubert[12]

$$
\begin{align}
T_c &= 9,5233\exp(-0,0009314PEMe - 0,544442d15 + 0,00064791 \times PEMe \times d15) \times \\
&\quad \times PEMe^{0,81067}d15^{0,53691} \tag{6.20}
\end{align}
$$

$$
\begin{align}
P_c &= 31958000000\exp(-0,008505PEMe - 4,8014d15 + 0,005749 \times PEMe \times d15) \times \\
&\quad \times PEMe^{-0,4844}d15^{4,0846} \tag{6.21}
\end{align}
$$

Riazi[12]

$$
\begin{align}
T_c &= 35,9413\exp(-0,00069PEMe - 1,4442d15 + 0,000491 \times PEMe \times d15) \times \\
&\quad \times PEMe^{0,7293}d15^{1,2771} \tag{6.22}
\end{align}
$$

6.1.4 Acentric Factor

Lee-Kesler method [11]

$$
\omega = \frac{-\ln\frac{P_c}{1,10325} - 5,92714 + 6,09648/T_{br} + 1,28862\ln T_{br} - 0,169347T_{br}^6}{15,2518 - 15,6875/T_{br} - 13,472\ln T_{br} + 0,43577T_{br}^6} \tag{6.23}
$$

Korsten[12]

$$
\omega = 0,5899 \times ((PEMV/T_c)^{1,3})/(1 - (PEMV/T_c)^{1,3}) \times \log(P_c/101325) - 1 \tag{6.24}
$$

6.1.5 Vapor Pressure

Lee-Kesler method[11]

$$
\begin{aligned}
\ln P_r^{pv} \ = \ & 5,92714 - 6,09648/T_{br} - 1,28862 \ln T_{br} + 0,169347 T_{br}^6 + \qquad (6.25) \\
& + \omega(15,2518 - 15,6875/T_{br} - 13,4721 \ln T_{br} + 0,43577 T_{br}^6),
\end{aligned}
$$

where

P_r^{pv} Reduced vapor pressure, P^{pv}/P_c

T_{br} Reduced NBP, T_b/T_c

ω Acentric factor

6.1.6 Viscosity

Letsou-Stiel [8]

$$
\begin{aligned}
\eta \ &= \ \frac{\xi_0 + \xi_1}{\xi} & (6.26) \\
\xi_0 \ &= \ 2,648 - 3,725 T_r + 1,309 T_r^2 & (6.27) \\
\xi_1 \ &= \ 7,425 - 13,39 T_r + 5,933 T_r^2 & (6.28) \\
\xi \ &= \ 176 \left(\frac{T_c}{MM^3 P_c^4} \right)^{1/6} & (6.29)
\end{aligned}
$$

where

η Viscosity (Pa.s)

P_c Critical pressure (bar)

T_r Reduced temperature, T/T_c

MM Molecular weight (kg/kmol)

Abbott[12]

$$
\begin{aligned}
t_1 \ = \ & 4,39371 - 1,94733 Kw + 0,12769 Kw^2 + 0,00032629 API^2 - 0,0118246 Kw API + \\
& + (0,171617 Kw^2 + 10,9943 API + 0,0950663 API^2 - 0,869218 Kw API \qquad (6.30) \\
\log v_{100} \ = \ & \frac{t_1}{API + 50,3642 - 4,78231 Kw}, \qquad\qquad\qquad\qquad\qquad\qquad\qquad (6.31)
\end{aligned}
$$

$$
\begin{aligned}
t_2 \ = \ & -0,463634 - 0,166532 API + 0,000513447 API^2 - 0,00848995 API Kw + \\
& + (0,080325 Kw + 1,24899 API + 0,19768 API^2 \qquad\qquad\qquad\qquad (6.32) \\
\log v_{210} \ = \ & \frac{t_2}{API + 26,786 - 2,6296 Kw}, \qquad\qquad\qquad\qquad\qquad\qquad\qquad (6.33)
\end{aligned}
$$

where

v_{100} Viscosity at 100 °F (cSt)

v_{210} Viscosity at 210 °F (cSt)

K_w Watson characterization factor

API Oil API degree

6.2 Hypothetical Components

The majority of properties of the hypothetical components is calculated, when necessary, using the group contribution methods, with the UNIFAC structure of the hypo as the basis of calculation. The table 4 lists the properties and their calculation methods.

Table 4: Hypo calculation methods.

Property	Symbol	Method
Critical temperature	T_c	Joback [8]
Critical pressure	P_c	Joback [8]
Critical volume	V_c	Joback [8]
Normal boiling point	T_b	Joback [8]
Vapor pressure	P^{pv}	Lee-Kesler (Eq. 6.25)
Acentric factor	ω	Lee-Kesler (Eq. 6.23)
Vaporization enthalpy	ΔH_{vap}	Vetere [8]
Ideal gas heat capacity	C_p^{gi}	Harrison-Seaton [13]
Ideal gas enthalpy of formation	ΔH_f^{298}	Marrero-Gani [14]

7 Other Properties

7.1 True Critical Point

The Gibbs criteria for the true critical point of a mixture of n components may be expressed of various forms, but the most convenient when using a pressure explicit cubic equation of state is

$$L = \begin{vmatrix} A_{11} & A_{12} & \ldots & A_{1n} \\ A_{21} & A_{22} & & \\ \vdots & & & \\ A_{n1} & \ldots & \ldots & A_{nn} \end{vmatrix} = 0 \tag{7.1}$$

$$M = \begin{vmatrix} A_{11} & A_{12} & \ldots & A_{1n} \\ A_{21} & A_{22} & & \\ \vdots & & & \\ A_{n-1,1} & \ldots & \ldots & A_{n-1,n} \\ \frac{\partial L}{\partial n_1} & \ldots & \ldots & \frac{\partial L}{\partial n_n} \end{vmatrix} = 0, \tag{7.2}$$

where

$$A_{12} = \left(\frac{\partial^2 A}{\partial n_1 \partial n_2} \right)_{T,V} \tag{7.3}$$

All the A terms in the equations 7.1 and 7.2 are the second derivatives of the total Helmholtz energy $\underline{A}$ with respect to mols and constant T and V. The determinants expressed by 7.1 and 7.2 are simultaneously solved for the critical volume and temperature. The critical pressure is then found by using the original EOS.

DWSIM utilizes the method described by Heidemann and Khalil [15] for the true critical point calculation using the *Peng-Robinson* and *Soave-Redlich-Kwong* equations of state.

7.2 Natural Gas Hydrates

The models for natural gas hydrates equilibrium calculations are mostly based in statistical thermodynamics to predict in which temperature and pressure conditions there will be formation or dissociation of hydrates. In these conditions,

$$f_w^i = f_w^H, \tag{7.4}$$

that is, the fugacity of water in hydrate is the same as in the water in any other phase present at equilibria.

The difference in the models present in DWSIM is mainly in the way that water fugacity in the hydrate phase is calculated. In the modified van der Waals and Platteeuw model, the isofugacity criteria is used indirectly through chemical potentials, which must also be equal in the equilibria:

$$\mu_w^i = \mu_w^H \tag{7.5}$$

remembering that

$$f_i = x_i P \exp((\mu_i - \mu_i^{gi})/RT). \tag{7.6}$$

7.2.1 Modified van der Waals and Platteeuw (Parrish and Prausnitz) method

The classic model for determination of equilibrium pressures and temperatures was developed by van der Waals and Platteeuw. This model was later extended by Parrish and Prausnitz [16] to take into account multiple "guests" in the hydrate structures. The condition of equilibrium used in the *vdwP* model is the equality of the chemical potential of water in the hydrate phase and in the other phases, which can be liquid, solid or both.

Chemical potential of water in the hydrate phase   In the modified var der Waals method, the chemical potential of water in the hydrate phase is calculated by:

$$\mu_w^H = \mu_w^\beta + RT \sum_m \nu_m \ln(1 - \sum_j \theta_{mj}), \tag{7.7}$$

where μ_w^β is the chemical potential of water in the empty hydrate lattice (something like an "ideal" chemical potential) and ν_m is the number of m cavities by water molecule in the lattice. The fraction of cavities *m-type* cavities occupied by the gaseous component l is

$$\theta_{ml} = (C_{ml} f_i)/((1 + \sum_j C_{mj} f_j)), \tag{7.8}$$

where C_{mj} is the Langmuir constant and fi is the fugacity of the gaseous component l. The Langmuir constant takes into account the interactions between the gas and the molecules of water in the cavities. Using the Lennard-Jones-Devonshire cell theory, van der Waals e Platteeuw showed that the Langmuir constant can be given by

$$C(T) = 4\pi/kT \int_0^\infty \exp[(-w(r))/kT] r^2 dr, \tag{7.9}$$

where T is the absolute temperature, k is the Boltzmann constant and *w(r)* is the spherically symmetric potential which is a function of the cell radius, the coordination number and the nature of the gas-water interaction. In this method, the Kihara potential with a spherical core is used,

$$w(r) = 2ze[\sigma^{12}/(R^{11}r)(\delta^{10} + a/R\delta^{11}) - \sigma^6/(R^5 r)(\delta^4 + a/R\delta^5)], \tag{7.10}$$

$$\delta^N = [(1 - r/R - a/R)^{-N}) - (1 + r/R - a/R)^{-N})]/N, \tag{7.11}$$

where N is equal to 4, 5, 10 or 11; z and R are, respectively, the coordination number and the cavity cell radius.

Supported hydrate formers   CH4, C2H6, C3H8, iC4H10, H2S, N2 and CO2.

Model applicability range   Temperature: 211 to 303 K; Pressure: 1 to 600 atm.

7.2.2 Klauda and Sandler

The model proposed by Klauda and Sandler [17] uses spherically symmetric Kihara potentials determined from viscosity data and the second virial coefficient, in opposition to the traditional models which adjust these parameters to experimental hydrate data. In general, this method predicts hydrate formation data more precisely than the other models.

Fugacity of water in the hydrate phase

$$
\begin{aligned}
f_w^H &= \exp(A_g^\beta \ln T + (B_g^\beta)/T + 2,7789 + D_g^\beta T) \times \\
&\quad \exp V_w^\beta [P - \exp(A_g^\beta \ln T + (B_g^\beta)/T + 2,7789 + D_g^\beta T)]/RT \times \\
&\quad \exp[\sum_m \nu_m \ln(1 - \sum_j (C_{ml}f_l)/(1 + \sum C_{mj}f_j))]
\end{aligned}
\tag{7.12}
$$

The A, B and D constants are specific for each hydrate former and represent the vapor pressure of the component in the empty hydrate lattice. V_w^β represents the basic hydrate molar volume (without the presence of guests) and the Langmuir constant (C) is calculated by the following equation:

$$
C(T) = 4\pi/kT \int_0^{R-a} \exp[(-w(r))/kT]r^2 dr
\tag{7.13}
$$

In the Klauda e Sandler method the spherically symmetric Kihara potential is also used,

$$
w(r) = 2ze[\sigma^{12}/(R^{11}r)(\delta^{10} + a/R\delta^{11}) - \sigma^6/(R^5 r)(\delta^4 + a/R\delta^5)]
\tag{7.14}
$$

$$
\delta^N = [(1 - r/R - a/R)^{-N}) - (1 + r/R - a/R)^{-N})]/N
\tag{7.15}
$$

with a modifications in the potential to include the effects of the second and third cell layers,

$$
w(r) = w(r)^{[1]}) + w(r)^{[2]}) + w(r)^{[3]}).
\tag{7.16}
$$

Supported hydrate formers   CH4, C2H6, C3H8, iC4H10, H2S, N2 and CO2.

Model applicability range   Temperature: 150 to 320 K; Pressure: 1 to 7000 atm

7.2.3 Chen and Guo

Chen and Guo [18] developed a model based in a formation mechanism based in two steps, the first being a quasi-chemical reaction to form the "basic hydrate" and the second as being a small gas absorption process in the linking cages of the basic hydrate. The results showed that this model is capable of predict hydrate formation conditions for pure gases and mixtures.

Fugacity of water in the hydrate phase   In the Chen and Guo model, a different approximation is used for the equilibrium condition. Here the equilibrium is verified by means of an isofugacity criteria of the hydrate formers in the hydrate and vapor phase. The fugacity of the component in the vapor phase is calculated by:

$$f_i^H = f_i^0 (1 - \theta_i)^{\alpha}, \tag{7.17}$$

where α depends on the structure of the hydrate formed, and

$$f_i^0 = f^0(P) f^0(T) f^0(x_w \gamma_w), \tag{7.18}$$

$$f^0(P) = exp(\beta P / T), \tag{7.19}$$

$$f^0(T) = A' exp(B' / (T - C')), \tag{7.20}$$

$$f^0(x_w \gamma_w) = (x_w \gamma_w)^{(-1/\lambda_2)}, \tag{7.21}$$

where β and λ_2 depend on the structure of the hydrate formed and A', B' and C' depends on the hydrate former. x_w and γ_m are, respectively, the water molar fraction and activity coefficient in the liquid phase.

In the Chen and Guo model, the Langmuir constants are calculated with an Antoine-type equation with parameters obtained from experimental data, for a limited range of temperature:

$$C(T) = X \exp(Y / (T - Z)) \tag{7.22}$$

Supported hydrate formers   CH4, C2H6, C3H8, iC4H10, H2S, N2, CO2 and nC4H10.

Model applicability range   Temperature: 259 to 304 K, Pressure: 1 to 700 atm.

7.3 Petroleum Cold Flow Properties

7.3.1 Refraction Index

API Procedure 2B5.1

$$
\begin{aligned}
I \quad = \quad & 0,02266 \exp(0,0003905 \times (1,8 MeABP) + 2,468 SG - 0,0005704(1,8 MeABP) \times SG) \times \\
& \times (1,8 MeABP)^{0,0572} SG^{-0,72}
\end{aligned}
\tag{7.23}
$$

$$r = \left(\frac{1 + 2I}{1 - I} \right)^{1/2} \tag{7.24}$$

where

r Refraction Index

SG Specific Gravity

$MeABP$ Mean Averaged Boiling Point (K)

7.3.2 Flash Point

API Procedure 2B7.1

$$PF = \{[0,69 \times ((t_{10ASTM} - 273,15) \times 9/5 + 32) - 118,2] - 32\} \times 5/9 + 273,15 \quad (7.25)$$

where

PF Flash Point (K)

t_{10ASTM} ASTM D93 10% vaporized temperature (K)

7.3.3 Pour Point

API Procedure 2B8.1

$$PFL = [753 + 136(1 - \exp(-0,15v_{100})) - 572SG + 0,0512v_{100} + 0,139(1,8MeABP)]/1,8$$
$$(7.26)$$

where

PFL Pour Point (K)

v_{100} Viscosity @ 100 °F (cSt)

7.3.4 Freezing Point

API Procedure 2B11.1

$$PC = -2390,42 + 1826SG + 122,49K - 0,135 \times 1,8 \times MeABP \quad (7.27)$$

where

PC Freezing Point (K)

K API characterization factor (API)

7.3.5 Cloud Point

API Procedure 2B12.1

$$PN = \left[10^{(-7,41+5,49\log(1,8MeABP)-0,712\times(1,8MeABP)^{0,315}-0,133SG)}\right]/1,8 \quad (7.28)$$

where

PN Cloud Point (K)

7.3.6 Cetane Index

API Procedure 2B13.1

$$\begin{aligned} IC = {} & 415,26 - 7,673API + 0,186 \times (1,8MeABP - 458,67) + 3,503API \times \\ & \times \log(1,8MeABP - 458,67) - 193,816 \times \log(1,8MeABP - 458.67) \quad (7.29) \end{aligned}$$

where

IC Cetane Index

API API degree of the oil

7.4 Chao-Seader Parameters

The Chao-Seader parameters needed by the CS/GS models are the Modified Acentric Factor, Solubility Parameter and Liquid Molar Volume. When absent, the Modified Acentric Factor is taken as the normal acentric factor, either read from the databases or calculated by using the methods described before in this document. The Solubility Parameter is given by

$$\delta = \left(\frac{\Delta H_v - RT}{V_L} \right)^{1/2} \tag{7.30}$$

where

ΔH_v Molar Heat of Vaporization

V_L Liquid Molar Volume at 20 °C

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