Preface

This book accompanies the ChemSep program, which was developed to allow students to do separation calculations on ordinary personal computers. This book is not a guide where we show how to use ChemSep (see the ChemSep user manual for that) but it is intended to supply technical background to help the user in his selection of models and correlations. It is hoped that sensible selections can be made by providing information on, descriptions of, and references to the models and correlations that are employed in ChemSep. Although we have tried to be as extensive as possible, it is impossible to describe all models and their underlaying theory, so references are given for further reading. There are probably many more literature models and correlations than are available in ChemSep, but we have tried to be as comprehensive as we could. Sometimes a choice had to be made in which models to implement without having any criteria to discriminate between models. Furthermore, not all models are applicable to a particular regime of operation. We try to adapt ChemSep as much as possible to comply with all model limitations and user requirements. This book serves as a replacement for the “manual” information files that we used to distribute with ChemSep. Therefore, some parts of this document might still be incomplete or unorganized and any suggestions or remarks are welcome. Of course, any remarks on the ChemSep program are welcome as well.

This book is written in \LaTeX, a complete typesetting language, and set in the standard Times-Roman 11 point font. It is also provided with ChemSep in ASCII text form (file CHEMSEP.TXT) for online reference which was generated with a \LaTeX to ASCII converter. The conversion is limited, with the result that the ASCII text file contains some unconverted \LaTeX formatting. A PostScript file (BOOK.PS) also generated by \LaTeX can be downloaded from our ftp site.

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Ross Taylor
Acknowledgements

Many people have helped to shape ChemSep. The project was started in 1988 at Delft University (The Netherlands) by Harry Koolijman, Arno Haket and Ross Taylor. The purpose was to make an interactive interface for doing equilibrium stage calculations on the PC platform. It had to be easy enough for use by students with little computer exposure and yet sufficiently comprehensive to solve the various problems encountered in a course on separation processes.

We would like to express our appreciation to Professor Hans Wesselings (now at the University of Groningen, the Netherlands) who initially promoted the project and made various resources available and encouraged us by letting students use the program for their course work. This has been an indispensable source of feedback that has helped us to improve the program. We also like to thank Peter Verheijen for his enthusiasm and contributions in the early years of the project. Also, various students have worked on projects to check and improve the programs and documentation, which was very helpful. Finally, ChemSep owes its very existence to the Internet which enabled the authors to keep in touch and continue development while living on different continents.
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Chapter 1

Solving Nonlinear Equations

In this chapter we discuss the methods employed in ChemSep to solve the separation problems at hand. Side-issues such as how to start an iterative method or how ChemSep solves the resulting linear system of equations also pass the review.

1.1 Newton’s method

ChemSep uses Newton’s method to solve the system of (MESH) equations derived from the flash or column problems. Newton’s method is a Simultaneous Correction (SC) method that each time corrects all the variables. To use it, the equations to be solved are written in the form

\[ F(x) = 0 \]  

(1.1)

where \( F \) is a vector consisting of all the equations to be solved and \( x \) is, again, the vector of variables. A Taylor series expansion of the function vector around the point \( x_o \) which the functions are evaluated gives (ignoring second and higher order terms):

\[ F(x) = F(x_o) + J(x - x_o) \]  

(1.2)

where \( J \) is the Jacobian matrix of partial derivatives of \( F \) with respect to the independent variables \( x \):

\[ J_{ij} = \frac{\partial F_i}{\partial x_j} \]  

(1.3)

If \( x \) is the actual solution to the system of equations, then \( F(x) = 0 \) and we can rewrite the above equation as:

\[ J(x - x_o) = -F(x_o) \]  

(1.4)

This linear system of equations may be solved for a new estimate of the vector \( x \). If the new vector, \( x \), obtained in this way does not actually satisfy the set of equations, \( F \), then
the procedure can be repeated using the calculated \( x \) as a new \( x \). The entire procedure is summarized below.

1. Set iteration counter, \( k \), to zero, estimate \( x_0 \)

2. Solve linearized equations for \( x_{k+1} \)

3. Check for convergence; if not obtained, increment \( k \) and return to step 2.

Solving the linear system does not require a full matrix inversion of the Jacobian and is normally done with Gaussian elimination or some type of decomposition technique. If the Jacobian has a lot of zero entries (i.e. it is sparse) then the linear system can be much more efficiently solved by using a sparse linear solver. For Jacobians with specific structures special solvers can be employed which are more efficient than a complete elimination or decomposition.

One very important property of the Newton's method is that the convergence is scale invariant and independent of the ordering of the equations. This means that the same convergence is obtained if one of the equations is multiplied by some number or if the equations are reordered in a different manner. This is very important, because this means we are free to order the equations to obtain a special Jacobian which might enable the use of a special solver. It also makes the method applicable to a wider range of problems and without requiring the user to scale equations or variables.

An important drawback of the Newton's method can be its sensitivity to the initial guess, \( x_0 \), since quadratic convergence is only achieved "close" to the solution. In order to obtain convergence, Newton's method requires that reasonable initial estimates be provided for all independent variables. It is obviously impractical to expect the user of a SC method to guess this number of quantities. Thus, the designer of a computer code implementing a SC method must provide one or more methods of generating initial estimates of all the unknown variables. Several techniques have been developed to improve the convergence away from the solution and to prevent the method from taking a step in a wrong direction. The simplest and most common technique is to "damp" the step of each variable to some range or fraction of the Newton step. However, this damping also reduces the method's effectiveness.

Simultaneous correction procedures have shown themselves to be generally fast and reliable, having a locally quadratic convergence rate in the case of Newton's method, and these methods are much less sensitive to difficulties associated with nonideal problems than are tearing methods. They also lend themselves to be easier extended with optimization, parametric sensitivity, or continuation methods.
1.2 Continuation method

A simple implementation of a continuation method is incorporated in ChemSep for more difficult problems. Continuation methods use a parameter to make a path from a known solution for a simplified model to the desired solution of the complete model. For example, the Newton homotopy starts with the initial guess as model and follows the path to the solution of the real problem by solving

\[ 0 = (1 - t)(F(X_0) - F(X)) + tF(X) \]  \hspace{1cm} (1.5)

where \( t \) varies from 0 (where \( X = X_0 \)) to 1 (where \( F(X) = 0 \)). Better continuation methods can be formulated while using a parameter which has some physical significance. In separations problems the most appropriate choice would be the degree to which mass transfer (between the present phases) prevails. In the equilibrium model the stage efficiency and in the nonequilibrium model the mass transfer rates represent this degree. Thus, they will be multiplied with a parameter \( t \) which will vary from 0 (no separation at all) to 1 (actual separation).
Chapter 2

Property Models

This chapter discusses the thermodynamic and physical property models available in ChemSep. The selection of these models can be quite important for the results produced by ChemSep. Most formulae are repeated here but additional reading is available in two main sources:


References are in between parentheses, by combining the letter A or B with the page number, for example (A43). The model ”types” are grouped by ChemSep menu.

2.1 Thermodynamic Properties

2.1.1 K-value models

*Ideal* (A251,B548) K-values for ideal mixtures are given by Raoult’s law:

\[ K_i = \frac{P_{\text{vap},i}}{P} \]  \hspace{1cm} (2.1)

*EOS* (A319,B301) K-values are calculated from the ratio of fugacity coefficients:

\[ K_i = \frac{\phi_i^L}{\phi_i^V} \]  \hspace{1cm} (2.2)
where the fugacity coefficients are calculated from an equation of state. This model is recommended for separations involving mixtures of hydrocarbons and light gases (hydrogen, carbondioxide, nitrogen, etc.) at low and high pressures. It is not recommended for nonideal chemical mixtures at low pressures. The EOS must be able to predict vapour as well as liquid fugacity coefficients.

*Gamma-Phi (A250,B301)* K-Values are calculated from:

\[
K_i = \frac{\gamma_i \phi_i^* P_i^* P F_i}{\phi_i^* P}
\]  
(2.3)

This option should be used when dealing with nonideal fluid mixtures. It should not be selected for separations at high pressures.

*DECHEMA (B301)* K-values are calculated from a simplified form of the complete Gamma-Phi model in which the vapour phase fugacity coefficient and Poynting correction factor are assumed equal to unity:

\[
K_i = \frac{\gamma_i P_i^*}{P}
\]  
(2.4)

This is the form of the K-value model used in the DECHEMA compilations of equilibrium data (Hence the name given to this menu option). DECHEMA uses the Antoine equation to compute the vapour pressures but ChemSep allows you to choose other vapour pressure models if you wish. This option should be used when dealing with non-ideal fluid mixtures. It should not be selected for separations at high pressures.

*Chao-Seader (B303)* The Chao-Seader method is widely used for mixtures of hydrocarbons and light gases. It is not recommended for nonideal mixtures. The method uses the Regular solution model for the liquid phase and the Redlich Kwong EOS for the vapour phase. An alternative choice would be the Equation of State option.

*Polynomial (B11)* Calculate K-value as function of the absolute temperature (Kelvin):

\[
K_i^{1/m_i} = A_i + B_i T + C_i T^2 + D_i T^3 + E_i T^4
\]  
(2.5)

You must supply the coefficients \( A \) through \( E \) and the exponent \( m \).

### 2.1.2 Activity coefficient models

Here we discuss the activity coefficient models available in ChemSep. For an in-depth discussion of these models see the standard references. For the calculation of activity coefficients and their derivatives (for diffusion calculations) see also Kooijman and Taylor (1991).

*Ideal* For an ideal system the activity coefficient of all species is unity, and thus, \( \ln \gamma_i = 0 \).
Regular (A284,B217) The regular solution model is due to Scatchard and Hildebrand. It is probably the simplest model of liquid mixtures. The model uses the Flory-Huggins modification. The activity coefficient is given by:

\[ \theta_i = \frac{V_i}{\sum_k x_k V_k} \]  
\[ \ln \gamma_i^* = \frac{V_i}{RT} \left[ \delta_i - \sum_j x_j \delta_j \theta_j \right]^2 \]  
\[ \ln \gamma_i = \ln \gamma_i^* + \ln \theta_i + 1 - \theta_i \]

where \( \delta_i \) is called the solubility parameter and \( V_i \) the molal volume of component \( i \) (both read from the PCD-file). This regular model is also incorporated in the Chao-Seader method of estimating \( K \)-values.

Margules (A256,B184) The "Three suffix" or two parameter form of the Margules equation is implemented in ChemSep:

\[ \ln \gamma_i = [A_{ij} + 2(A_{ji} - A_{ij})x_i x_j] x_j^2 \]

It can only be used for binary mixtures (\( i=1, j=2 \) and \( i=2, j=1 \)).

Van Laar (A256,B189) The Van Laar equation is

\[ \ln \gamma_i = \frac{A_{ij}}{\left(1 + \frac{A_{ij} x_i}{A_{ji} x_j}\right)^2} \]

It can only be used for binary mixtures (\( i=1, j=2 \) and \( i=2, j=1 \)).

Wilson (A274,B192) The Wilson equation was proposed by G.M. Wilson in 1964. It is a "two parameter equation". That means that two interaction parameters per binary pair are needed to estimate the activity coefficients in a multicomponent mixture. For mixtures that do NOT form two liquids, the Wilson equation is, on average, the most accurate of the methods used to predict equilibria in multicomponent mixtures (Reference B). However, for aqueous mixtures the NRTL model is usually superior.

\[ A_{ij} = \left( \frac{V_j}{V_i} \right) \exp \left( -\frac{(\mu_{ij} - \mu_{ii})}{RT} \right) \]
\[ S_i = \sum_{j=1}^{c} x_j A_{ij} \]
\[ \ln \gamma_i = -\ln(S_i) - \sum_{k=1}^{c} x_k A_{ki}/S_k \]

The two interaction parameters are \( (\mu_{ij} - \mu_{ii}) \) and \( (\mu_{ji} - \mu_{ii}) \) per binary pair of components.
**NRTL** (A274,B201) The NRTL equation due to Renon and Prausnitz is a three parameter equation. Unlike the original Wilson equation it may also be used for liquid-liquid equilibrium calculations.

\[
\tau_{ij} = \frac{(g_{ij} - g_{ii})}{RT} \quad (2.14)
\]

\[
G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (2.15)
\]

\[
S_i = \sum_{j=1}^{c} x_j G_{ji} \quad (2.16)
\]

\[
C_i = \sum_{j=1}^{c} x_j G_{ji}\tau_{ji} \quad (2.17)
\]

\[
\ln \gamma_i = \frac{C_i}{S_i} + \sum_{k=1}^{c} x_k G_{ik}(\tau_{ik} - C_k/S_k)/S_k \quad (2.18)
\]

The interaction parameters are \((g_{ij} - g_{ii}), (g_{ji} - g_{ki})\), and \(\alpha_{ij}\) per binary (only one \(\alpha\) is required as \(\alpha_{ij} = \alpha_{ji}\)).

**UNIQUAC** (A274,B205) UNIQUAC stands for Universal Quasi Chemical and is a very widely used model of liquid mixtures that reduces, with certain assumptions, to almost all of the other models mentioned in the list. Like the Wilson equation, it is a two parameter equation but is capable of predicting liquid-liquid equilibria as well as vapour-liquid equilibria. Two types of UNIQUAC models are available Original and q-prime. Original is the default option and is to be used if you have obtained interaction parameters from DECHEMA. The q-prime (q') form of UNIQUAC is recommended for alcohol mixtures. An additional pure component parameter, q', is needed. If q' equals the q value it reduces to the original method.

\[
r = \sum_{i=1}^{c} x_i r_i \quad (2.19)
\]

\[
q = \sum_{i=1}^{c} x_i q_i \quad (2.20)
\]

\[
\phi = \frac{x_i r_i}{r} \quad (2.21)
\]

\[
\theta = \frac{x_i r_i}{r} \quad (2.22)
\]

\[
\tau_{ji} = \exp(-\left(\lambda_{ji} - \lambda_{ii}\right)/RT) \quad (2.23)
\]

\[
S_i = \sum_{j=1}^{c} \theta_j \tau_{ji} \quad (2.24)
\]

\[
\ln \gamma_i^e = \left(1 - \frac{z}{2} q_i^e\right) \ln \left(\frac{\phi_i}{x_i}\right) + \frac{z}{2} q_i^e \ln \left(\frac{\theta_i}{x_i}\right) - \frac{r_i}{r} + \frac{z}{2} q^e \left(\frac{r_i}{r} - \frac{q_i}{q}\right) \quad (2.25)
\]

\[
\ln \gamma_i^r = q_i \left(1 - \ln(S_i) - \sum_{k=1}^{c} \frac{\theta_{k}\tau_{ik}}{S_k}\right) \quad (2.26)
\]

\[
\ln \gamma_i = \ln \gamma_i^e + \ln \gamma_i^r \quad (2.27)
\]
The interaction parameters are \((\lambda_{ij} - \lambda_{ii})\) and \((\lambda_{ji} - \lambda_{ii})\) per binary. The parameters \(r_i\) and \(q_i\) are read from the component database (PCD file).

**UNIFAC** (A314,B219) UNIFAC is a group contribution method that is used to predict equilibria in systems for which NO experimental equilibrium data exist. The method is based on the UNIUQUAC equation, but is completely predictive in the sense that it does not require interaction parameters. Instead, these are computed from group contributions of all the molecules in the mixture. If you select one of the other models but fail to specify a complete set of the interaction parameters, then UNIFAC is used to compute any unspecified parameters.

**ASOG** (A313,B219) ASOG is a group contribution method similar to UNIFAC but based on the Wilson equation. It was developed before UNIFAC but is less widely used because of the comparative lack of fitted group interaction parameters.

### 2.1.3 Vapour pressure models

**Antoine** (A208,B11) The Antoine Equation is:

\[
\ln P_i^* = A_i - \frac{B_i}{T + C_i}
\]  

(2.28)

Note the natural logarithm. This option should be selected if you are using activity coefficient models with parameters from the DEHEMA series. Antoine parameters are available in the ChemSep data files and need not be loaded.

**Extended Antoine** (B11) The Extended Antoine equation incorporated in ChemSep’s thermodynamic routines is:

\[
\ln P_i^* = A_i + \frac{B_i}{C_i + T} + D_i T + E_i \ln T + F_i T_i^G
\]  

(2.29)

The parameters \(A\) through \(G\) must be supplied by the user. A library of parameters for some common chemicals is provided with ChemSep in the file EANTOINE.LIB.

**DIPPR** (B11) The Design Institute for Physical Property Research (DIPPR) has recently published a correlation for the vapour pressure.

\[
\ln P_i^* = A_i + \frac{B_i}{T} + D_i T + C_i \ln T + D_i T_i^E
\]  

(2.30)

DIPPR parameters \(A-E\) are also available in ChemSep data files.

**Riedel** (B523) The Riedel equation is best suited to nonpolar mixtures:

\[
\zeta_T = 36/T_T + 96.7 \log T_T - 35 - T_T^6
\]  

(2.31)

\[
\zeta_{T_0} = 36/T_{T_0} + 96.7 \log T_{T_0} - 35 - T_{T_0}^6
\]  

(2.32)

\[
\phi = 0.118 \zeta_T - 7 \log T_T
\]  

(2.33)
\begin{align}
\psi &= 0.0364\zeta_T - \log T_r \\
\alpha &= \frac{0.136\zeta_{Tb} + \log P_c - 5.01}{0.0364\zeta_{Tb} - \log T_{rb}} \\
\log P^*_r &= -\phi - (\alpha - 7)\psi
\end{align}

Lee-Kesler (A207,B69) Lee and Kesler used a Pitzer expansion to obtain:

\begin{align}
\ln P^*_i &= f^{(0)} + \omega_i f^{(1)} \\
f^{(0)} &= 5.92714 - \frac{6.09648}{T_r} - 1.28862\ln T_r + 0.169347T_r^6 \\
f^{(1)} &= 15.2518 - \frac{15.6875}{T_r} - 13.4721\ln T_r + 0.435777T_r^6
\end{align}

where \( T_r = T/T_{Ci} \). Both the Riedel and Lee-Kesler models are recommended for hydrocarbon mixtures in particular.

2.1.4 Equations of State (EOS)

Three types of equations of state may be selected in \textit{ChemSep}: \textit{Ideal Gas}, \textit{Virial}, and \textit{Cubic EOS}. The fugacity coefficient of an ideal gas mixture (B3) is unity (since the fugacity represents the deviation from an ideal gas, and we use the natural logarithm of the fugacity as the fugacity coefficient). The pressure relation for an ideal gas is:

\begin{equation}
P = \frac{RT}{V}
\end{equation}

The Virial and cubic EOS are discussed in the sections below.

2.1.5 Virial EOS

\textit{Hayden-O’Connell} (B39) Hayden and O’Connell have provided a method of predicting the second virial coefficient for multicomponent vapour mixtures. The method is quite complicated (see Prausnitz \textit{et al.}, 1980) but is well suited to ideal and nonideal systems at low pressures. You must input the association parameters. A library of association parameters is provided with \textit{ChemSep} in the file HAYDENO.IPD.

\textit{Tsonopoulous} (B45) The two-term virial equation:

\begin{equation}
P = \frac{RT}{V} + \frac{BRT}{V}
\end{equation}

The method of Tsonopoulous for estimating virial coefficients is recommended for hydrocarbon mixtures at low pressures. It is based on an earlier correlation due to
Pitzer.

\[
B = \sum_{i=1}^{c} \sum_{j=1}^{c} y_i y_j B_{ij}
\]  

(2.42)

\[
B_{ij} = RT_{c,ij} P_{c,ij} \left( B_{ij}^{(0)} + \omega_{ij} B_{ij}^{(1)} \right)
\]  

(2.43)

\[
B_{ij}^{(0)} = 0.1445 - \frac{0.33}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8}
\]  

(2.44)

\[
B_{ij}^{(1)} = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.0008}{T_r^8}
\]  

(2.45)

\[
\omega_{ij} = \frac{\omega_i + \omega_j}{2}
\]  

(2.46)

\[
Z_{c,ij} = \frac{Z_{ci} + Z_{cj}}{2}
\]  

(2.47)

\[
V_{c,ij}^{1/3} = \frac{V_{ci}^{1/3} V_{cj}^{1/3}}{2}
\]  

(2.48)

\[
T_{c,ij} = (1 - k_{ij}) \sqrt{T_{ci} T_{cj}}
\]  

(2.49)

\[
P_{c,ij} = \frac{Z_{c,ij} RT_{c,ij}}{V_{c,ij}}
\]  

(2.50)

Binary interaction parameters \( k_{ij} \) must be supplied by the user. For paraffins \( k_{ij} \) can be calculated with:

\[
k_{ij} = 1 - \frac{8 \sqrt{V_{ci} V_{cj}}}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3}
\]  

(2.51)

**DIPPR** The Design Institute for Physical Property Research (DIPPR) has published a correlation for the second virial coefficient, see the section on physical properties below. The parameters for the DIPPR correlation are also available in *ChemSep* (PCD) data files.

**Chemical theory** This is an extension on the Hayden O’Connell virial model, which takes the association of molecules into account (see Prausnitz *et al.*, 1980). Since the mole fractions are a function of the association, an iterative method (here Newton’s method) must be used to obtain them in order to compute the virial coefficients.

### 2.1.6 Cubic EOS

**Van der Waals** (A43,B15) The Van der Waals (VdW) Equation was the first cubic equation of state. The basic equation has served as a starting point for many other EOS. The VdW equation cannot be used to determine properties of liquid phases, thus it may not be selected for the EOS K-value model.

\[
P = \frac{RT}{V - b} - \frac{a}{V^2}
\]  

(2.52)
with

\[ a_i = \frac{27RT_i^2}{64P_{ci}} \]  

(2.53)

\[ b_i = \frac{RT_{ci}}{8P_{ci}} \]  

(2.54)

and the mixing rules:

\[ a = \sum_{i=1}^{c} \sum_{j=1}^{c} y_i y_j a_{ij} \]  

(2.55)

\[ a_{ij} = \sqrt{a_i a_j} \]  

(2.56)

\[ b = \sum_{i=1}^{c} y_i b_i \]  

(2.57)

*Redlich Kwong* (A43,B43) The Redlich Kwong (RK) equation is used in the Chao-Seader method of computing thermodynamic properties. The RK equation cannot be used to determine properties of liquid phases, thus it cannot be selected for the EOS K-value model.

\[
P = \frac{RT}{V - b} - \frac{a}{\sqrt{TV(V + b)}}
\]

(2.58)

with

\[ a_i = \frac{\Omega_a R^2 T_{2.5}^2}{P_{ci}} \]  

(2.59)

\[ \Omega_a = 0.42748 \]  

(2.60)

\[ b_i = \frac{\Omega_b RT_{ci}}{P_{ci}} \]  

(2.61)

\[ \Omega_b = 0.08664 \]  

(2.62)

and the mixing rules:

\[ a = \sum_{i=1}^{c} \sum_{j=1}^{c} y_i y_j a_{ij} \]  

(2.63)

\[ a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \]  

(2.64)

\[ b = \sum_{i=1}^{c} y_i b_i \]  

(2.65)

where \( k_{ij} \) is a binary interaction parameter (original RK: \( k_{ij} = 0 \)).

*Soave Redlich Kwong* (A43,B52) Soave’s modification of the Redlich Kwong (SRK) EOS is one of the most widely used methods of computing thermodynamic properties. The SRK EOS is most suitable for computing properties of hydrocarbon mixtures.

\[
P = \frac{RT}{V - b} - \frac{a}{V(V + b)}
\]

(2.66)
with

\[
\begin{align*}
    a_i &= a_i(T_{ci})\alpha(T_{ri}, \omega_i) \\
    a_i(T_{ci}) &= \frac{\Omega_a R^2 T_{ci}^2}{P_{ci}} \\
    \Omega_a &= 0.42747 \\
    \alpha(T_{ri}, \omega_i) &= \left[ 1 + (0.48508 + 1.55171\omega_i - 0.15613\omega_i^2)(1 - \sqrt{T_{ri}}) \right]^2 \\
    b_i &= \frac{\Omega_b R T_{ci}}{P_{ci}} \\
    \Omega_b &= 0.08664
\end{align*}
\]

and the mixing rules:

\[
\begin{align*}
    a &= \sum_{i=1}^{c} \sum_{j=1}^{c} y_i y_j a_{ij} \\
    a_{ij} &= (1 - k_{ij})\sqrt{a_i a_j} \\
    b &= \sum_{i=1}^{c} y_i b_i
\end{align*}
\]

\textit{API SRK EOS} (B53) Graboski and Daubert have modified the coefficients in the SRK EOS and provided a special relation for hydrogen. This modification of the SRK EOS has been recommended by the American Petroleum Institute (API), hence the name of this menu option. It uses the same equations as the SRK except for the \( \alpha \):

\[
\alpha(T_{ri}, \omega_i) = \left[ 1 + (0.48508 + 1.55171\omega_i - 0.15613\omega_i^2)(1 - \sqrt{T_{ri}}) \right]^2
\]

and specially for hydrogen:

\[
\alpha(T_{ri}, \omega_i) = 1.202e^{-0.50288T_{ri}}
\]

\textit{Peng Robinson EOS} (A43,B54) The Peng-Robinson equation is another cubic EOS that owes its origins to the RK and SRK EOS. The PR EOS, however, gives improved predictions of liquid phase densities.

\[
P = \frac{RT}{V - b} \left[ 1 - \frac{a}{V(V + b) + b(V - b)} \right]
\]

with

\[
\begin{align*}
    a_i &= a_i(T_{ci})\alpha(T_{ri}, \omega_i) \\
    a_i(T_{ci}) &= \frac{\Omega_a R^2 T_{ci}^2}{P_{ci}} \\
    \Omega_a &= 0.45724 \\
    \alpha(T_{ri}, \omega_i) &= \left[ 1 + (0.37464 + 1.5422\omega_i - 0.26992\omega_i^2)(1 - \sqrt{T_{ri}}) \right]^2 \\
    b_i &= \frac{\Omega_b R T_{ci}}{P_{ci}} \\
    \Omega_b &= 0.07880
\end{align*}
\]
and the mixing rules:

$$a = \sum_{i=1}^{c} \sum_{j=1}^{c} y_{ij} a_{ij}$$  \hspace{1cm} (2.85)

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j}$$  \hspace{1cm} (2.86)

$$b = \sum_{i=1}^{c} y_i b_i$$  \hspace{1cm} (2.87)

2.1.7 Enthalpy

None No enthalpy balance is used in the calculations. WARNING: the use of this model with subcooled and superheated feeds or for columns with heat addition or removal on some of the stages will give incorrect results. The heat duties of the condenser and reboiler will be reported as zero since there is no basis for calculating them.

Ideal (B152) In this model the enthalpy is computed from the ideal gas contribution. For liquids, the latent heat of vaporization is subtracted from the ideal gas contribution.

Excess (B518) This model includes the ideal enthalpy as above. The excess enthalpy is calculated from the activity coefficient model or the temperature derivative of the fugacity coefficients dependent on the choice of the model for the K-values, and is added to the ideal part.

Polynomial Vapour as well as liquid enthalpy are calculated as functions of the absolute temperature (K). Both the enthalpies use the following function:

$$H_i = A_i + B_i T + C_i T^2 + D_i T^3$$  \hspace{1cm} (2.88)

You must enter the coefficients A through E in the "Load Data" option of the Properties menu for vapour and liquid enthalpy for each component.

2.2 Physical Properties

A number of different polynomials is implemented in ChemSep to evaluate physical properties over a certain temperature range. These temperature correlations are assigned a unique number in the range of 0-255 (see Table 2.1). For each up to 5 parameters (A-E) are available. Table 2.2 shows which pure component properties can be modeled with temperature correlations and their typical correlation number.

All types of equations may be used for any of the physical properties but, of course, some formulas were specifically developed for prediction of particular properties. Besides the parameters A-E the temperature limits of the correlation must also be present. If the
Table 2.1: Temperature correlations

<table>
<thead>
<tr>
<th>Equation number</th>
<th>Parameter(s)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>A,B</td>
<td>$A + BT$</td>
</tr>
<tr>
<td>3</td>
<td>A-C</td>
<td>$A + BT + CT^2$</td>
</tr>
<tr>
<td>4</td>
<td>A-D</td>
<td>$A + BT + CT^2 + DT^3$</td>
</tr>
<tr>
<td>10</td>
<td>A-C</td>
<td>$\exp \left( A - \frac{B}{C + T} \right)$</td>
</tr>
<tr>
<td>100</td>
<td>A-E</td>
<td>$A + BT + CT^2 + DT^3 + ET^4$</td>
</tr>
<tr>
<td>101</td>
<td>A-E</td>
<td>$\exp \left( A + \frac{B}{C} + CT + DT + ET \right)$</td>
</tr>
<tr>
<td>102</td>
<td>A-D</td>
<td>$A + B\exp \left( -\frac{C}{T} \right)$</td>
</tr>
<tr>
<td>103</td>
<td>A-D</td>
<td>$A + B\exp \left( -\frac{C}{T} \right)$</td>
</tr>
<tr>
<td>104</td>
<td>A-E</td>
<td>$A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \frac{E}{T^4}$</td>
</tr>
<tr>
<td>105</td>
<td>A-D</td>
<td>$A \left[ 1 + C/T + D/T^2 \right]$</td>
</tr>
<tr>
<td>106</td>
<td>A-E</td>
<td>$A (1 - T/\gamma) / (B + CT + DT^2 + ET^3)$</td>
</tr>
<tr>
<td>107</td>
<td>A-E</td>
<td>$A + B\left( \frac{\gamma}{\gamma/\sinh(\gamma)} \right)^2 + D\left( \frac{\gamma}{\gamma/\cosh(\gamma)} \right)^2$</td>
</tr>
</tbody>
</table>

Temperature specified falls out of the temperature range of a correlation (or the temperature limits are missing/incomplete) normally an alternative (default) method will be used automatically.

Physical properties models can be selected manually or the automatic selection can be used (which is the default). Below we discuss the models for calculating physical properties for pure components and mixtures, for vapour or liquid phases. ChemSep uses an automatic selection when no model is selected at all and the selection is left as *'s. Depending on range, phase, conditions, data availability, and required property ChemSep will make a guess of the best model to use. ChemSep does allow you to pick default models, and will use them if the model’s range is valid. In case a property cannot be computed with a specific model it will use an estimation method or a fixed estimate (it is a good habit to check predicted physical properties when possible).

Certain methods require mixture (critical) properties, commonly used mixing rules are:

$$T_{c,m} = \sum_{i=1}^{c} x_i T_{c,i}$$  \hspace{1cm} (2.89)

$$V_{c,m} = \sum_{i=1}^{c} x_i V_{c,i}$$  \hspace{1cm} (2.90)

$$Z_{c,m} = \sum_{i=1}^{c} x_i Z_{c,i}$$  \hspace{1cm} (2.91)

$$P_{c,m} = \frac{Z_{c,m} RT_{c,m}}{V_{c,m}}$$  \hspace{1cm} (2.92)
### Table 2.2: Component properties with the typical correlation number

<table>
<thead>
<tr>
<th>Property</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid density</td>
<td>105</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>101</td>
</tr>
<tr>
<td>Heat of vaporisation</td>
<td>106</td>
</tr>
<tr>
<td>Liquid heat capacity</td>
<td>100</td>
</tr>
<tr>
<td>Ideal gas heat capacity</td>
<td>107</td>
</tr>
<tr>
<td>Second virial coefficient</td>
<td>104</td>
</tr>
<tr>
<td>Liquid viscosity</td>
<td>101</td>
</tr>
<tr>
<td>Vapour viscosity</td>
<td>102</td>
</tr>
<tr>
<td>Liquid thermal conductivity</td>
<td>100</td>
</tr>
<tr>
<td>Vapour thermal conductivity</td>
<td>102</td>
</tr>
<tr>
<td>Surface tension</td>
<td>106</td>
</tr>
<tr>
<td>Ideal gas heat capacity (Reid Prausnitz and Poling)</td>
<td>4</td>
</tr>
<tr>
<td>Antoine</td>
<td>10</td>
</tr>
<tr>
<td>Liquid viscosity (Reid, Prausnitz and Sherwood)</td>
<td>2</td>
</tr>
</tbody>
</table>

### Table 2.3: Default physical property correlations

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture liquid density</td>
<td>Rackett</td>
</tr>
<tr>
<td>Component liquid density</td>
<td>Polynomial</td>
</tr>
<tr>
<td>Vapour density</td>
<td>Cubic EOS</td>
</tr>
<tr>
<td>Mixture liquid viscosity</td>
<td>Molar averaging</td>
</tr>
<tr>
<td>Component vapour viscosity</td>
<td>Polynomial/Letso-Stiel</td>
</tr>
<tr>
<td>Mixture vapour viscosity</td>
<td>Brokaw</td>
</tr>
<tr>
<td>Component vapour viscosity</td>
<td>Polynomial</td>
</tr>
<tr>
<td>Mixture liquid thermal conductivity</td>
<td>Molar average</td>
</tr>
<tr>
<td>Component liquid thermal conductivity</td>
<td>Polynomial</td>
</tr>
<tr>
<td>Mixture vapour thermal conductivity</td>
<td>Molar average</td>
</tr>
<tr>
<td>Component vapour thermal conductivity</td>
<td>Polynomial/9B-3</td>
</tr>
<tr>
<td>Liquid diffusivity</td>
<td>Kooijman-Taylor/Wilke-Chang</td>
</tr>
<tr>
<td>Vapour diffusivity</td>
<td>Fuller et al.</td>
</tr>
<tr>
<td>Mixture surface tension</td>
<td>Molar average</td>
</tr>
<tr>
<td>Component surface tension</td>
<td>Polynomial</td>
</tr>
<tr>
<td>Liquid-Liquid interfacial tension</td>
<td>Jufu et al.</td>
</tr>
</tbody>
</table>
\[ M_m = \sum_{i=1}^{c} x_i M_i \]  

which will be referred as the "normal" mixing rules. Reduced properties will be calculated by:

\[ T_r = \frac{T}{T_c} \]  
\[ P_r = \frac{P}{P_c} \]  
\[ V_r = \frac{V}{V_c} \]

unless specified otherwise.

### 2.2.1 Liquid density

Mixture liquid densities (in \text{kmol/m}^3) are calculated with:

**Equation of State** The previously discussed Peng-Robinson equation of state is used to calculate the mixture compressibility directly from pure component critical properties and mixture parameters, from which the density can be calculated easily. Use this method if some components in the mixture are supercritical.

**Amagat's law**

\[ \frac{1}{\rho_m^L} = \sum_{i=1}^{c} \frac{x_i}{\rho_i^L} \]  

where the component liquid densities, \( \rho_i^L \), are computed as discussed below.

**Rackett (A67,89)** This is DIPPR procedure 4B, which requires component critical temperatures, pressures, mole weights and Rackett parameters (for which critical compressibilities are used if unknown):

\[ T_{c,m} = \sum_{i=1}^{c} x_i T_{c,i} \]  
\[ Z_{R,m} = \sum_{i=1}^{c} x_i Z_{R,i} \]  
\[ T_r = \frac{T}{T_{c,m}} \]  
\[ F_z = Z_{R,m}^{(1+(1-T_r)^{2/7})} \]  
\[ A = \sum_{i=1}^{c} \frac{x_i T_{c,i}}{M_i P_{c,i}} \]  
\[ \rho_m^L = \frac{1}{ARF_z} \sum_{i=1}^{c} x_i M_i \]
If the reduced temperature, \( T_r \), is greater than unity a default value of 50 \( \text{kmol/m}^3 \) is used.

Yen-Woods Mixture critical temperature, volume, and compressibility are calculated with the "normal" mixing rules. If the reduced temperature, \( T_r = T/T_{c,m} \), is greater than unity a default value of 50 \( \text{kmol/m}^3 \) is used, otherwise the density is calculated from:

\[
T_s = (1 - T_r)^{1/3} \quad (2.104)
\]

\[
A = 17.4425 - 214.578Z_c + 989.625 \times Z_c^2 - 1522.06Z_c^3 \quad (2.105)
\]

\[
Z_c \leq 0.26 : B = -3.28257 + 13.6377Z_c + 107.4844Z_c^2 - 384.211Z_c^3 \quad (2.106)
\]

\[
Z_c > 0.26 : B = 60.20901 - 402.063Z_c + 501Z_c^2 + 641Z_c^3 \quad (2.107)
\]

\[
\rho_L^* = \frac{1 + AT_s + BT^2 + (0.93 - B)T^4}{V_c} \quad (2.108)
\]


\[
V_m^* = \frac{1}{4} \left( \sum_{i=1}^{c} x_i V_i^* + 3 \left( \sum_{i=1}^{c} x_i V_i^{*2/3} \right) \left( \sum_{i=1}^{c} x_i V_i^{*1/3} \right) \right) \quad (2.109)
\]

\[
T_{c,m} = \sum_{i=i}^{c} \sum_{j=j}^{c} x_i x_j V_{ij}^* T_{c,ij}/V_m^* \quad (2.110)
\]

\[
\omega_{SRK,m} = \sum_{i=1}^{c} x_i \omega_{SRK,i} \quad (2.111)
\]

\[
Z_{c,m} = 0.291 - 0.08 \omega_{SRK,i} \quad (2.112)
\]

\[
P_{c,m} = Z_{c,m} RT_{c,m}/V_m^* \quad (2.113)
\]

If the reduced temperature is larger than unity a default value of 50 \( \text{kmol/m}^3 \) is used, otherwise the saturated liquid volume (\( V_s \)) is calculated from:

\[
\frac{V_s}{V_m^*} = V_{R}^{[0]} (1 - \omega_{SRK,m} V_{R}^{[\delta]}) \quad (2.114)
\]

\[
V_{R}^{[0]} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \quad (2.115)
\]

\[
V_{R}^{[\delta]} = \frac{e + f T_r + g T_r^2 + h T_r^3}{(T_r - 1.00001)} \quad (2.116)
\]

\[
a = 1.52816 \quad e = 0.296123
\]

\[
b = 1.43907 \quad f = 0.386914
\]

\[
c = -0.81446 \quad g = 0.0427258
\]

\[
d = 0.190454 \quad h = 0.0480645
\]

The density equals the inverse of the liquid molar volume.

For the density of compressed liquids the saturated liquid volume is corrected (Thomson et al., AIChE J, 28, 671, 1982):

\[
V = V_s \left( 1 - c \ln \frac{\beta + P}{\beta + P_{vpm}} \right) \quad (2.117)
\]
\[
\begin{align*}
\beta/P_c &= -1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + d(1 - T_r) + e(1 - T_r)^{1/3} \quad (2.118) \\
e &= \exp(f + g\omega_{SRK,m} + h\omega_{SRK,m}^2) \quad (2.119) \\
c &= j + k\omega_{SRK} \quad (2.120)
\end{align*}
\]

where
\[
\begin{align*}
a &= 9.070217 & g &= 0.250047 \\
b &= 62.45326 & h &= 1.14188 \\
d &= -135.1102 & j &= 0.0861488 \\
f &= 4.79594 & k &= 0.0344483
\end{align*}
\]

and the vapour pressure is from the generalized Riedel equations:
\[
\begin{align*}
P_{vpm} &= P_{c,m}P_{rm} \quad (2.121) \\
\log P_{rm} &= P_{rm}^{[0]} + \omega_{SRK,m}P_{rm}^{[1]} \quad (2.122) \\
P_{rm}^{[0]} &= 5.8031817\log T_{rm} + 0.07608141\alpha \quad (2.123) \\
P_{rm}^{[1]} &= 4.86601\log T_{rm} + 0.0372175\alpha \quad (2.124) \\
\alpha &= 35 - 36/T_{rm} - 96.736\log T_{rm} + T_{rm}^6 \quad (2.125) \\
T_{rm} &= T/T_{c,m} \quad (2.126)
\end{align*}
\]

This method should be used for reduced temperatures from 0.25 up to the critical point.

Pure component liquid densities are computed from the Peng-Robinson EOS for temperatures above a component's critical temperature, otherwise with one of the following methods:

**Polynomial** When within the temperature range, a polynomial is the default way for calculating component liquid densities.

**Rackett** This is the DIPPR procedure 4A:
\[
\begin{align*}
F_z &= \frac{P_{c,1}^{1+(1-T_r)^{2/7}}}{P_{c,1}} \quad (2.127) \\
\rho_m^L &= \frac{P_{c,c}/RT_c}{F_z} \quad (2.128)
\end{align*}
\]

**COSTALD** Hankinson and Thompson method described as above but with pure component parameters.

The pure component liquid densities are corrected for pressure effects with the correction of Thomson et al. (1982) as described for the Hankinson and Thompson method for mixtures.

### 2.2.2 Vapour density

Vapour densities are computed with the equation of state selected for the thermodynamic properties (possible selections are *Ideal gas EOS*, *Virial EOS*, and *Cubic EOS*).
2.2.3 Liquid Heat Capacity

The mixture liquid heat capacity is the molar average of the component liquid heat capacities, which are generally computed from a temperature correlation. Alternatively the liquid heat capacity could be computed from a corresponding states method and the ideal gas capacity. Rowlinson (1969, see A410) proposed a Lee-Kesler heat capacity departure function which was later modified to:

\[
C_{p,i}^{L} - C_{p}^{ig} = 1.45 + 0.45(1 - T_{r})^{-1} + 0.25\omega \left[ 17.11 + 25.2(1 - T_{r})^{1.3}T_{r}^{-1} + 1.742(1 - T_{r})^{-1} \right]
\]

(2.129)

However, in ChemSep the temperature correlation is used for all temperatures to prevent problems arising from using different liquid heat capacity methods in the same column (which especially trouble nonequilibrium models). Liquid heat capacities could also be computed from the selected thermodynamic models to circumvent this problem.

2.2.4 Vapour Heat Capacity

The mixture vapour heat capacity is the molar average of the component vapour heat capacities, which are computed from the ideal gas heat capacity (RPP) 4 parameter temperature correlation. If no parameters for this correlation are present, the vapour heat capacity temperature correlation is used (if within the temperature range).

2.2.5 Liquid Viscosity

Mixture liquid viscosity are computed from DIPPR procedure 8H from the pure component liquid viscosities from:

\[
\ln \eta_{m}^{L} = \sum_{i=1}^{c} z_{i} \ln \eta_{i}^{L}
\]

(2.130)

where \(z_{i}\) are either the mole fractions (for molar averaging, the default) or alternatively the weight fractions for mass averaging. A better method is from Teja and Rice (1981, A479). However, this method requires interaction parameters. Here a different mixing rule (for \(T_{ci}V_{ci}\)) is used which improves the model predictions with unity interaction coefficients:

\[
\omega_{m} = \sum_{i=1}^{c} x_{i}\omega_{i}
\]

(2.131)

\[
M_{m} = \sum_{i=1}^{c} x_{i} M_{i}
\]

(2.132)

\[
V_{cm} = \sum_{i=1}^{c} \sum_{j=1}^{c} x_{i}x_{j} V_{cij}
\]

(2.133)
\[ V_{cij} = \frac{(V_{ci}^{1/3} + V_{cj}^{1/3})^3}{8} \]  

\[ T_{cm} = \frac{\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j T_{cij} V_{cij}}{V_{cm}} \]  

\[ T_{cij} V_{cij} = \psi_{ij} \frac{T_{ci} V_{ci} + T_{cj} V_{cj}}{2} \]

where \( \psi_{ij} \) is set to unity for all components. The liquid viscosity of the mixture is computed from two reference components

\[ \ln(\epsilon_m \eta_m) = \ln(\epsilon_1 \eta_1) + \left[ \ln(\epsilon_2 \eta_2) - \ln(\epsilon_1 \eta_1) \right] \left( \frac{\omega_m - \omega_i}{\omega_2 - \omega_1} \right) \]

with \( \epsilon \) defined as

\[ \epsilon_i = \frac{V_{ci}^{2/3}}{\sqrt{T_{ci} M_i}} \]

and the reference component viscosities are evaluated at \( TT_{ci}/T_{cm} \). Component liquid viscosities are calculated from the liquid viscosity temperature correlation if the temperature is within the valid range. Otherwise the component viscosity is computed with DIPPR procedure 8G, the Letson-Stiel method (1973, see A471):

\[ \xi = \frac{2173.424T_{ci}^{1.8}}{\sqrt{M_i P_{ci}^{2/3}}} \]

\[ \xi^{[0]} = (1.5174 - 2.135T_r + 0.75T_r^2)10^{-5} \]  

\[ \xi^{[1]} = (4.2552 - 7.6747T_r + 3.4T_r^2)10^{-5} \]  

\[ \eta_i^L = (\xi^{[0]} + \omega \xi^{[1]})/\xi \]

Alternatively the simple temperature correlation given in Reid et al. (RPS liquid viscosity, see A439) can be used:

\[ \log \eta = A + B/T \]

A high pressure correction by Lucas (A436) is used to correct the influence of the pressure on the liquid viscosity:

\[ \eta = \frac{1 + D(\Delta P_r/2.118)^A}{1 + C \omega_i \Delta P_r^C} \eta_{SL} \]

where \( \eta_{SL} \) is the viscosity of the saturated liquid at \( P_{vp} \), and

\[ \Delta P_r = (P - P_{vp})/P_{ci} \]

\[ A = 0.9991 - [4.674 \times 10^{-4}/(1.0523T_r^{0.03877} - 1.0513)] \]  

\[ C = -0.07921 + 2.1616T_r - 13.4040T_r^2 + 44.1706T_r^3 \]

\[ -84.8291T_r^4 + 96.12097T_r^5 - 59.8127T_r^6 + 15.6719T_r^7 \]

\[ D = [0.3257/(1.0039 - T_r^{2.573}0.2906) - 0.2086 \]
2.2.6 Vapour Viscosity

Mixture vapour viscosities are computed using DIPPR procedure 8D-1 from component viscosities as follows:

\[ \eta_m^L = \sum_{i=1}^{c} \frac{x_i \eta_i^L}{\sum x_i \phi_{ij}} \]  

(2.150)

where the interaction parameters \( \phi_{ij} \) can be calculated by Wilke’s (1950) method:

\[ \phi_{ij} = \left( \frac{1 + \sqrt{\eta_i/\eta_j(M_i/M_j)^{1/4}}}{\sqrt{8(1 + M_i/M_j)}} \right)^2 \]  

(2.151)

or by Brokaw’s method:

\[ \phi_{ij} = \frac{4}{(1 + M_i/M_j)(1 + M_i/M_j)} \]  

(2.152)

\[ sm = \frac{4}{(1 + M_i/M_j)(1 + M_i/M_j)} \]  

(2.153)

\[ A = \frac{sm}{M_i/M_j} \left( 1 + \frac{(M_i/M_j - (M_i/M_j)^{0.45})}{2(1 + M_i/M_j)} + \frac{(1 + (M_i/M_j)^{0.45})}{\sqrt{sm(1 + M_i/M_j)}} \right) \]  

(2.154)

If the Lennard-Jones energy parameter, \( \epsilon \) (in Kelvin), and the Stockmayer’s polar parameter, \( \delta \), are known, \( S \) is calculated from:

\[ S = \frac{1 + \sqrt{(T/\epsilon_i)(T/\epsilon_j)} + \delta_i \delta_j / 4}{\sqrt{1 + T/\epsilon_i + \delta_i^2 / 4} \sqrt{1 + T/\epsilon_j + \delta_j^2 / 4}} \]  

(2.155)

otherwise it is approximated by \( S = 1. \) \( \epsilon \) and \( \delta \) can be estimated from:

\[ \epsilon = 65.3T_c z_{c,i}^{3.6} \]  

(2.156)

\[ \delta = 1.744 \times 10^9 \mu^2 \frac{V_b i T_b}{V_b i T_b} \]  

(2.157)

Where \( \mu \) is the dipole moment in Debye. Vapour viscosities are a function of pressure and a correction is normally applied. Mixture properties are computed with the “normal” mixing rules. DIPPR procedure 8E can be used to compute the high pressure viscosity:

\[ \rho_c = 1/V_c \]  

(2.158)

\[ \rho_r = \rho / \rho_c \]  

(2.159)

\[ \xi = 2173.4241 T_c^{1/6} c_{m,c} m \frac{P_{c,c}^{2/3}}{M_m P_{c,m} c_{c,m}} \]  

(2.160)

\[ A = \exp(1.4439 \rho_r) - \exp(-1.111 \rho_r^{1.85}) \]  

(2.161)

\[ B = 1.08 \times 10^{-7} A / \xi \]  

(2.162)

\[ \eta_{hp} = \eta + B \]  

(2.163)
Table 2.4: Constants for the Yoon-Thodos method

<table>
<thead>
<tr>
<th>Hydrogen</th>
<th>Helium</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>a=47.65</td>
<td>a=52.57</td>
<td>a=46.1</td>
</tr>
<tr>
<td>b=0.657</td>
<td>b=0.656</td>
<td>b=0.618</td>
</tr>
<tr>
<td>c=20.0</td>
<td>c=18.9</td>
<td>c=20.4</td>
</tr>
<tr>
<td>d=0.858</td>
<td>d=1.144</td>
<td>d=0.449</td>
</tr>
<tr>
<td>e=-19.0</td>
<td>e=17.9</td>
<td>e=19.4</td>
</tr>
<tr>
<td>f=-3.995</td>
<td>f=-5.182</td>
<td>f=-4.058</td>
</tr>
</tbody>
</table>

where $\rho$ is the vapour mixture molar density.

Both Wilke’s and Brokaw’s method require pure component viscosities. These are normally obtained from the vapour viscosity temperature correlations, as long as the temperature is within the valid temperature range. If not, then the viscosity can be computed with the Chapman-Enskog kinetic theory (see Hirschfelder et al., 1954 and A391-393):

\[ T^* = T/\epsilon \]
\[ \Omega_v = a(T^*)^{-b} + c/\exp(dT^*) + e/\exp(f T^*) \]
\[ \eta_V = 26.69 \times 10^{-7}MT/\sigma^2(\Omega_v + 0.2\delta^2/T^*) \]

where the collision integral constants are $a = 1.16145$, $b = 0.14874$, $c = 0.52487$, $d = 0.77320$, $e = 2.16178$, and $f = 2.43787$. The viscosity may also be computed with the Yoon and Thodos method (DIPPR procedure 8B):

\[ \xi_i = 2173.4241T_{c,i}^{1/6}/\sqrt{M_iP_{c,i}^{2/3}} \]
\[ \eta_i^V = \frac{1 + aT_r^b - c\exp(dT_r - r) + e\exp(fT_r)}{10^8} \]

where the constants $a - f$ are given in Table 2.4.

Another method for calculating the vapor viscosity is the Lucas (A397) method:

\[ \eta = 10^{-7}[0.807T_r^{0.618} - 0.357\exp(-0.449T_r) + 0.340\exp(-4.058T_r) + 0.018]F_p^\alpha F_q^\alpha/\xi \]
\[ \xi = 0.176 \left( \frac{T_c}{M^3(10^{-5}P_c)^4} \right)^{1/6} \]

where $F_p^\alpha$ and $F_q^\alpha$ are polarity and quantum correction factors. The polarity correction depends on the reduced dipole moment:

\[ \mu_r = \frac{52.46(\mu/3.336 \times 10^{-30})^2(10^{-5}P_c)}{T_c^2} \]
If $\mu_r$ is smaller than 0.022 then the correction factor is unity, else if it is smaller than 0.075 it is given by
\[
F_p^o = 1 + 30.55(0.292 - Z_c)^{1.72}
\] (2.173)
else by
\[
F_p^o = 1 + 30.55(0.292 - Z_c)^{1.72}[0.96 + 0.1(T_r - 0.7)]
\] (2.174)
The quantum correction is only used for quantum gases He, H$_2$, and D$_2$,
\[
F_q^o = 1.22Q^{0.15} \left( 1 + 0.00385[(T_r - 12)^2]^{1/4}\text{sign}(T_r - 12) \right)
\] (2.175)
where $Q = 1.38$ (He), $Q = 0.76$ (H$_2$), $Q = 0.52$ (D$_2$). There is also a specific correction for high pressures (A421) by Lucas.
\[
\eta = Y F_p F_q \eta^o
\] (2.176)
\[
Y = 1 + \frac{aP_r^e}{bF_r + (1 + cF_r^d)^{-1}}
\] (2.177)
\[
F_p = \frac{1 + (F_p^o - 1)Y^{-3}}{F_p^o}
\] (2.178)
\[
F_q = \frac{1 + (F_q^o - 1)[Y^{-1} - 0.007(\ln Y)^4]}{F_q^o}
\] (2.179)
where $\eta^o$ refers to the low-pressure viscosity (note that the original Lucas method has a different rule for Y if $T_r$ is below unity, however, this introduces a discontinuity which is avoided here). The parameters $a$ through $f$ are evaluated with:
\[
a = 1.245 \times 10^{-3} \frac{10^{-3}}{T_r} \times \text{exp}5.1726T_r^{0.3286}
\] (2.180)
\[
b = a(1.6553T_r - 1.2723)
\] (2.181)
\[
c = 0.4489 \frac{10^{-3}}{T_r} \times \text{exp}3.0578T_r^{-37.7332}
\] (2.182)
\[
d = 1.7368 \frac{10^{-3}}{T_r} \times \text{exp}2.2310T_r^{-7.6351}
\] (2.183)
\[
e = 1.3088
\] (2.184)
\[
f = 0.9425 \times 0.1853T_r^{0.4489}
\] (2.185)
where, in case $T_r$ is below unity, $T_r$ is taken to be unity. For mixtures the Lucas model uses the following mixing rules:
\[
T_{cm} = \sum_{i=1}^{c} y_i T_{ci}
\] (2.186)
\[
V_{cm} = \sum_{i=1}^{c} y_i V_{ci}
\] (2.187)
\[
Z_{cm} = \sum_{i=1}^{c} y_i Z_{ci}
\] (2.188)
\[ P_{cm} = \frac{RT_{cm} Z_{cm}}{V_{cm}} \]  
\[ M_m = \sum_{i=1}^{c} y_i M_i \]  
\[ F_{pm}^o = \sum_{i=1}^{c} y_i F_{pi}^o \]  
\[ F_{qm}^o = A \sum_{i=1}^{c} y_i F_{qi}^o \]

where \( A \) is a correction factor depending on the molecular weights of the components in the mixture. Let \( H \) denote the component of highest molecular weight and \( L \) of lowest, then if \( M_H/M_L > 9 \):

\[ A = 1 - 0.01(M_H/M_L)^{0.57} \]  
else \( A = 1 \). The mixture vapor viscosity is computed with the Lucas method as for a component which has the mixture properties \( T_m, P_m, M_m, F_{pm}^o \), and \( F_{qm}^o \). Therefore, the method is not interpolative in the same way as the techniques of Wilke and Brokaw (that is, the method does not necessarily lead to pure component viscosity \( \eta_i \) when all \( y_j = 0 \) except \( y_i = 1 \)).

### 2.2.7 Liquid Thermal Conductivity

The mixture liquid thermal conductivity \( \lambda_m^L (W/mK) \), can be computed using the following methods from the component liquid thermal conductivities:

#### Molar average
This is the default method (and the simplest):

\[ \lambda_m^L = \sum_{i=1}^{c} x_i \lambda_i^L \]  

#### DIPPR procedure 9I

\[ F_{v,i} = x_i / \sum_{i=1}^{c} x_i / \rho_i^L \]  
\[ \lambda_{ij} = \frac{2}{1/\lambda_i + 1/\lambda_j} \]  
\[ \lambda_m^L = \sum_{i=1}^{c} \sum_{j=1}^{c} F_{v,i} F_{v,j} \lambda_{ij} \]

#### DIPPR procedure 9H

\[ \frac{1}{\sqrt{\lambda_m^L}} = \sum_{i=1}^{c} \frac{w_i}{(\lambda_i^L)^2} \]

where \( w_i \) is the weight fraction of component \( i \).
A correction is applied when the pressure is larger than 3.5 bar:

\[
\lambda_{hp} = \left(0.63T_r^{1.2}P_r/(30 + P_r) + 0.98 + 0.0079P_rT_r^{1.4}\right)\lambda
\]  

(2.200)

This is DIPPR procedure 9G-1 where the mixture parameters are computed by the "normal" mixing rules. Component liquid thermal conductivities are calculated from one of the following methods:

**Polynomial** The temperature correlation is normally used as long as the temperature is in the valid range and no other method is explicitly selected.

*Pachaiyappan et al.*

\[
f = 3 + 20(1 - T_r)^{2/3}
\]

(2.201)

\[
b = 3 + 20(1 - 273.15/T_{c,i})^{2/3}
\]

(2.202)

\[
\lambda_i = c10^{-4}M_i^{1/2}P_i^L(f/b)
\]

(2.203)

for straight chain hydrocarbons \(c = 1.811\) and \(x = 1.001\) else \(c = 4.407\) and \(x = 0.7717\).

*Latini et al.* This is DIPPR procedure 9E (see A549,550):

\[
\lambda_i^L = \frac{A(1 - T_r)^{0.38}}{T_r^{1.6}}
\]

(2.204)

\[
A = \frac{A^*T_h^a}{M_i^{3/2}T_c^s}
\]

(2.205)

where parameters \(A^*, \alpha, \beta, \) and \(\gamma\) depend on the class of the component as shown in Table 2.5.

### 2.2.8 Vapour Thermal Conductivity

**Molar average** The mixture vapour thermal conductivity is computed from the pure component thermal conductivities as follows:

\[
\lambda_m^V = \sum_{i=1}^c x_i\lambda_i^V
\]

(2.206)

**Kinetic theory** This is DIPPR procedure 9D:

\[
\lambda_m^V = \sum_{i=1}^c \frac{x_i\lambda_i^V}{\sum_{j=1}^c x_j\phi_{ij}}
\]

(2.207)

where interaction parameters \(\phi_{ij}\) are computed from:

\[
\phi_{ij} = 0.25(1 + \sqrt{\frac{\eta_i M_j T/T + 1.5 T_{b,i}}{\eta_j M_i T/T + 1.5 T_{b,j}}} \frac{T + \sqrt{1.5^2 T_{b,i} T_{b,j}}}{T + 1.5 T_{b,i}})
\]

(2.208)

Note that the component viscosities are required for this evaluation.
Table 2.5: Parameters for the Latini equation for liquid thermal conductivity

<table>
<thead>
<tr>
<th>Family</th>
<th>$A^*$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated hydrocarbons</td>
<td>0.0035</td>
<td>1.2</td>
<td>0.5</td>
<td>0.167</td>
</tr>
<tr>
<td>Olefins</td>
<td>0.0361</td>
<td>1.2</td>
<td>1.0</td>
<td>0.167</td>
</tr>
<tr>
<td>Cycloparaffins</td>
<td>0.0310</td>
<td>1.2</td>
<td>1.0</td>
<td>0.167</td>
</tr>
<tr>
<td>Aromatics</td>
<td>0.0346</td>
<td>1.2</td>
<td>1.0</td>
<td>0.167</td>
</tr>
<tr>
<td>Alcohols, phenols</td>
<td>0.00339</td>
<td>1.2</td>
<td>0.5</td>
<td>0.167</td>
</tr>
<tr>
<td>Acids (organic)</td>
<td>0.00319</td>
<td>1.2</td>
<td>0.5</td>
<td>0.167</td>
</tr>
<tr>
<td>Ketones</td>
<td>0.00383</td>
<td>1.2</td>
<td>0.5</td>
<td>0.167</td>
</tr>
<tr>
<td>Esters</td>
<td>0.0415</td>
<td>1.2</td>
<td>1.0</td>
<td>0.167</td>
</tr>
<tr>
<td>Ethers</td>
<td>0.0385</td>
<td>1.2</td>
<td>1.0</td>
<td>0.167</td>
</tr>
<tr>
<td>Refrigerants:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R20, R21, R22, R23</td>
<td>0.562</td>
<td>0.0</td>
<td>0.5</td>
<td>-0.167</td>
</tr>
<tr>
<td>Others</td>
<td>0.494</td>
<td>0.0</td>
<td>0.5</td>
<td>-0.167</td>
</tr>
</tbody>
</table>

If the system pressure is larger than 1 atmosphere a correction is applied according to DIPPR procedure 9C-1. Mixture parameters are computed using the "normal" mixing rules. Critical and reduced densities are computed from:

$$\rho_c = \frac{1}{V_{c,m}}$$

$$\rho_r = \frac{\rho}{\rho_c}$$

If the reduced density is below 0.5 then $a = 2.702$, $b = 0.535$, and $c = -1$; if the reduced density is within $[0.5, 2]$ then $a = 2.528$, $b = 0.67$, and $c = -1.069$; otherwise $a = 0.574$, $b = 1.155$, and $c = 2.016$. The high pressure thermal conductivity correction is then calculated from:

$$\Delta \lambda = \frac{a10^{-8}(\exp(b \rho_r) + c)}{(\frac{\sqrt{M_m \bar{V}^{1/6}_{c,m}}}{p_{c,m}^{1/6}})^{5/3}Z_{c,m}}$$

which must be added to the calculated thermal conductivity for low pressure.

Pure component vapour thermal conductivities are estimated from the following methods:

*Polynomial* The temperature correlation is normally used as long as the temperature is in the valid range and no other method is explicitly selected.

*DIPPR procedure 9B-3* This method is the default in case the temperature is out of the range of the temperature correlation:

$$\lambda^V_i = (1.15(C_p - R) + 16903.36)\eta^V_i/M_i$$
This method is recommended for linear molecules:

\[ \chi_V^Y = (1.3(C_p - R) + 14644 - 2928.8/T_r)\eta_i^Y/M_i \]  

(2.213)

**DIPPR procedure 9B-1** This method is suitable for monatomic gases only:

\[ \chi_V^Y = 2.5(C_p - R)\eta_i^Y/M_i \]  

(2.214)

*Misic-Thodos 2* This method is used for methane and cyclic compounds below \( T_r = 1 \):

\[
\xi = \frac{2173.424T_{c,i}^{1/6}}{\sqrt{M_iP_{c,i}^{2/3}}} \]  

(2.215)

\[
\lambda_i = 4.91 \times 10^{-7}T_rC_p/\xi \]  

(2.216)

*Misic-Thodos 1* This is the Misic-Thodos method for all other compounds:

\[
\xi = \frac{2173.424T_{c,i}^{1/6}}{\sqrt{M_iP_{c,i}^{2/3}}} \]  

(2.217)

\[
\lambda_i = 11.05 \times 10^{-8}(14.52T_r - 5.14)^{1/6}C_p/\xi \]  

(2.218)

### 2.2.9 Liquid Diffusivity

Generalized Maxwell-Stefan binary diffusion coefficients \( D_{ij} \) are computed from the Kooijman-Taylor (1990) correlation where

\[
D_{ij}^k = D_{ij}^o, \quad k = i \]  

(2.219)

\[
D_{ij}^k = D_{ji}^o, \quad k = j \]  

(2.220)

\[
D_{ij}^k = \sqrt{D_{ik}^oD_{jk}^o}, \quad k \neq i, k \neq j \]  

(2.221)

\[
D_{ij} = \sum_{k=1}^{c} D_{ij}^k \]  

(2.222)

Liquid binary infinitive diffusion coefficients \( (D_{ij}^o) \) are normally computed by the Wilke-Chang method unless selected otherwise. The following models are available:

**Wilke-Chang** This is DIPPR procedure 10-E proposed by Wilke and Chang (1955, see A598)

\[
D_{ab}^o = 1.1728 \times 10^{-16} \frac{\sqrt{\phi_b M_i T}}{\eta_b V_{b,a}^{0.6}} \]  

(2.223)

where \( \phi_b \) is association factor for the solvent (2.26 for water, 1.9 for methanol, 1.5 for ethanol and 1.0 for unassociated solvents).
This is DIPPR procedure 10-F for the diffusivity of solute $a$ in water proposed by Hayduk and Laudie (1974):

$$D_{aw}^o = 8.62 \times 10^{-14} \eta_w^{-1.14} V_{ba}^{0.589}$$  \hspace{1cm} (2.224)

Hayduk-Minas aqueous Estimates diffusivity of solute $a$ in water, proposed by Hayduk and Minhas (1982, see also A602):

$$D_{aw}^o = (3.36 V_{ba}^{-0.19} - 3.65)10^{-12} \eta_{wa}^{0.0958/V_{ba}^{0.12}} T^{1.52}$$  \hspace{1cm} (2.225)

Hayduk-Minas for non-aqueous systems Estimates diffusivity of solute $a$ in polar and non-polar solvent $b$ (which is not water), proposed by Hayduk and Minhas (1982, see also A603):

$$D_{ab}^o = 4.3637 \times 10^{-18} \eta_b^{-0.19} r_a^{0.2} r_b^{-0.4} T^{1.7}$$  \hspace{1cm} (2.226)

Hayduk-Minas paraffins Estimates diffusion coefficients for mixtures of normal paraffins from Hayduk-Minhas correlation equation 7 of their paper as corrected by Siddiqi and Lucas (1986, see also A602):

$$D_{ab}^o = 9.859 \times 10^{-14} V_{ba}^{-0.71} (1000\eta_{wb})^{0.0102/V_{ws}^{0.701}}$$  \hspace{1cm} (2.227)

Siddiqi-Lucas aqueous Estimates diffusivity of solute $a$ in water, proposed by Siddiqi and Lucas (1986):

$$D_{aw}^o = 5.6795 \times 10^{-16} V_{ba}^{-0.5173} \eta_w^{1.026} T$$  \hspace{1cm} (2.228)

Siddiqi-Lucas Estimates diffusivity of solute $a$ in solvent $b$ (not water), proposed by Siddiqi and Lucas (1986):

$$D_{ab}^o = 5.2383 \times 10^{-15} V_{ba}^{-0.45} V_{bb}^{0.265} \eta_b^{-0.907} T$$  \hspace{1cm} (2.229)

Umesi-Danner Estimates diffusivity of solute $a$ in solvent $b$:

$$D_{ab}^o = 5.927 \times 10^{-12} \frac{T r_b}{\eta_b r_a^{2/3}}$$  \hspace{1cm} (2.230)

Tyx-Calus correlation Estimates diffusivity of solute $a$ in solvent $b$ (see A600):

$$D_{ab}^o = 8.93 \times 10^{-12} \left(\frac{V_{ba}}{V_{bb}^2}\right)^{1/6} \left(\frac{P_b}{P_a}\right)^{0.6} \frac{T}{\eta_b}$$  \hspace{1cm} (2.231)

This method is not yet implemented!
### Fuller diffusion volumes

<table>
<thead>
<tr>
<th>Atomic and structural diffusion volume increments</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>15.9</td>
</tr>
<tr>
<td>H</td>
<td>2.31</td>
</tr>
<tr>
<td>O</td>
<td>6.11</td>
</tr>
<tr>
<td>N</td>
<td>4.54</td>
</tr>
<tr>
<td>Ring</td>
<td>-18.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diffusion volumes of simple molecules</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.67</td>
</tr>
<tr>
<td>Ne</td>
<td>5.98</td>
</tr>
<tr>
<td>Ar</td>
<td>16.2</td>
</tr>
<tr>
<td>Kr</td>
<td>24.5</td>
</tr>
<tr>
<td>Xe</td>
<td>32.7</td>
</tr>
<tr>
<td>H2</td>
<td>6.12</td>
</tr>
<tr>
<td>D2</td>
<td>6.84</td>
</tr>
<tr>
<td>N2</td>
<td>18.5</td>
</tr>
<tr>
<td>O2</td>
<td>16.3</td>
</tr>
<tr>
<td>Air</td>
<td>19.7</td>
</tr>
</tbody>
</table>

#### 2.2.10 Vapour Diffusivity

Generalized Maxwell-Stefan binary diffusion coefficients $D_{ij}$ are equal to the normal binary diffusion coefficients (since the gas is considered an ideal system for which the thermodynamic matrix is the identity matrix). Normally these are computed with the Fuller-Schettler-Giddings method (see A587) but if Fuller volume parameters are missing the Wilke-Lee modification of the Chapman-Enskog kinetic theory is used.

* Fuller et al. This is DIPPR procedure 10-A which was developed by Fuller et al. (1966,1969):

$$D_{ab}^V = 1.013 \times 10^{-2} T^{1.75} \sqrt{(1/M_a + 1/M_b)} P(\sqrt{V_a} + \sqrt{V_b})^2$$

(2.232)

where $V_a$ and $V_b$ are the Fuller molecular diffusion volumes which are calculated by summing the atomic contributions from Table 2.6. This table also lists some special diffusion volumes for simple molecules.

* Chapman-Enskog This is DIPPR procedure 10B which computes the binary gas diffusion coefficient from a simplified kinetic theory correlation. The average collision diameter and energy parameter are:

$$\sigma_{ab} = (\sigma_a + \sigma_b)/2$$

(2.233)

$$\epsilon_{ab} = \sqrt{\epsilon_a + \epsilon_b}$$

(2.234)
The diffusion collision integral is

$$T^* = \frac{T}{\epsilon_{ab}}$$  \hspace{1cm} (2.235)

$$\Omega_D = a(T^*)^{-b} + c/\exp(dT^*) + e/\exp(fT^*) + g/\exp(hT^*)$$  \hspace{1cm} (2.236)

where the collision integral constants are $a = 1.06036$, $b = 0.1561$, $c = 0.193$, $d = 0.47635$, $e = 1.03587$, $f = 1.52996$, $g = 1.76474$, and $h = 3.89411$. If Stockmayer polar parameters are known the integral gets corrected with:

$$\Omega_{D,c} = \Omega_D + \frac{0.19\delta_a \delta_b}{T^*}$$  \hspace{1cm} (2.237)

and the diffusion coefficient is

$$D_{ab}^V = C\frac{T^{3/2}\sqrt{M} + 1/M_b}{P\sigma_{ab}\omega_D}$$  \hspace{1cm} (2.238)

where constant $C = 1.883 \times 10^{-2}$.

**Wilke-Lee** Wilke and Lee (1955, see A587) proposed modified version of the kinetic theory method described above with

$$C = 2.1987 \times 10^{-2} - 5.07 \times 10^{-3} \sqrt{1/M_a + 1/M_b}$$  \hspace{1cm} (2.239)

### 2.2.11 Surface Tension

**Molar average** This is the default method:

$$\sigma_m = \sum_{i=1}^{c} x_i\sigma_i$$  \hspace{1cm} (2.240)

**Winterfeld et al.** This method by Winterfeld et al. (1978) is DIPPR 7C procedure:

$$\sigma_m = \frac{\sum_{i=1}^{c} \left( x_i/\rho_i^L \right)^2 + \sum_{j=1}^{c} x_i x_j \sqrt{\sigma_i \sigma_j \rho_i^L \rho_j^L} \right)}{\left( \sum_{i=1}^{c} x_i/\rho_i^L \right)^2}$$  \hspace{1cm} (2.241)

**Digulio-Teja** This method evaluates the component surface tensions at the components normal boiling points ($\sigma_{bi}$) and computes the mixture critical temperature, normal boiling temperature and the mixture surface tension at normal boiling temperature with the following mixing rules:

$$T_{c,m} = \sum_{i=1}^{c} x_i T_{c,i}$$  \hspace{1cm} (2.242)

$$T_{b,m} = \sum_{i=1}^{c} x_i T_{b,i}$$  \hspace{1cm} (2.243)

$$\sigma_{b,m} = \sum_{i=1}^{c} x_i \sigma_{b,i}$$  \hspace{1cm} (2.244)
Then it corrects the $\sigma, m$ with:

$$T^* = \frac{(1/T_r - 1)}{(1/T_{rb} - 1)}$$

$$\sigma = 1.002855(T^*)^{1.118091} \frac{T}{T_b} \sigma_r$$

Component surface tensions are only determined for temperatures below the component’s critical temperature, otherwise it is assumed that the component does not contribute to the mixture surface tension (i.e. $\sigma_i = 0$). The following methods are available:

**Polynomial** The temperature correlation is normally used as long as the temperature is in the valid range and no other method is explicitly selected.

**Brock-Bird** This is DIPPR procedure 7A:

$$T_{br} = \frac{T_{b,i}}{T_{c,i}}$$

$$Q = 0.1207 \left( \frac{1 + T_{br}(\ln(P_{c,i}) - 11.526)}{(1 - T_r)} \right) - 0.281$$

$$\sigma_i = 4.6 \times 10^{-7} P_{ci}^{2/3} T_{ci}^{1/3} (1 - T_r)^{11/9}$$

**Lielmezs-Herrick** This method by Lielmezs and Herrick (1986) uses the normal polynomial but evaluates it at the reduced normal boiling temperature and corrects the resulting $\sigma_r$ with:

$$T^* = \frac{(1/T_r - 1)}{(1/T_{rb} - 1)}$$

$$\sigma = 1.002855(T^*)^{1.118091} \frac{T}{T_b} \sigma_r$$

### 2.2.12 Liquid-Liquid Interfacial Tension

This property is only required for simulating Liquid-Liquid extractors with the nonequilibrium model. API method 10B3 uses the calculated surface tensions for both liquid phases and the interfacial tension, $\sigma'$, is computed from

$$\sigma' = \sigma_1 + \sigma_2 - 1.1 \sqrt{\sigma_1 \sigma_2}$$

This method generally overpredicts the interfacial tension for aqueous systems. We use a general method from Jufu et al. (1986):

$$X = -\ln(x'_1 + x'_2 + x_3)$$

$$\sigma' = \frac{KRTX}{A_{w0} \exp(X)(x'_1 q_1 + x'_2 q_2 + x_3 q_3)}$$
with $A_{w0} = 2.5 \times 10^5 \frac{m^2}{mol}$, $R = 8.3144 \frac{J}{mol/K}$, $K = 0.9414 (-)$, and $q_i$ is the UNIQUAC surface area parameters of the components $i$. The components are ordered in such a manner that component 1 and 2 are the dominating components in the two liquid phases. Then the rest of the components are lumped into one mole fraction, $x_3$. This lumped mole fraction is taken for the phase which has the largest $x_3$ (the richest). $q_3$ is the molar averaged $q$ for that phase for all components except 1 and 2.

**Symbol List**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a, b$</td>
<td>Cubic EOS parameters</td>
</tr>
<tr>
<td>$B$</td>
<td>Second virial coefficient ($m^3/kmol$)</td>
</tr>
<tr>
<td>$c$</td>
<td>Number of components</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Mass heat capacity ($J/kg.K$)</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>Binary diffusion coefficient ($m^2/s$)</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>Binary Maxwell-Stefan diffusion coefficient ($m^2/s$)</td>
</tr>
<tr>
<td>$D_{i}^{\omega}$</td>
<td>Infinite dilution binary diffusion coefficient ($m^2/s$)</td>
</tr>
<tr>
<td>$K_i$</td>
<td>K-value of component $i$, equilibrium ratio ($K_i = y_i/x_i$)</td>
</tr>
<tr>
<td>$k_{ij}$</td>
<td>Binary interaction coefficient (for EOS)</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular mass ($kg/kmol$)</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant = 8134 ($J/kmolK$)</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius of gyration (Angstrom)</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure ($Pa$)</td>
</tr>
<tr>
<td>$P^*$, $P_{vap}$</td>
<td>Vapour pressure ($Pa$)</td>
</tr>
<tr>
<td>$P_i$</td>
<td>Parachor ($m^3kg^{1/4}/s^{1/2}$) of component $i$</td>
</tr>
<tr>
<td>$PF$</td>
<td>Poynting correction</td>
</tr>
<tr>
<td>$q$</td>
<td>UNIQUAC surface area parameter</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature ($K$)</td>
</tr>
<tr>
<td>$T_r$</td>
<td>Reduced temperature ($T_r = T/T_c$)</td>
</tr>
<tr>
<td>$T_b$</td>
<td>Normal boiling temperature ($K$)</td>
</tr>
<tr>
<td>$V$</td>
<td>Molar volume ($m^3/kmol$)</td>
</tr>
<tr>
<td>$V_b$</td>
<td>Molar volume at normal boiling point ($m^3/kmol$)</td>
</tr>
<tr>
<td>$V_i$</td>
<td>Saturated molar volume ($m^3/kmol$)</td>
</tr>
<tr>
<td>$w$</td>
<td>Weight fraction (of component)</td>
</tr>
<tr>
<td>$x$</td>
<td>Liquid mole fraction (of component)</td>
</tr>
<tr>
<td>$y$</td>
<td>Vapour mole fraction (of component)</td>
</tr>
<tr>
<td>$Z$</td>
<td>Compressibility</td>
</tr>
<tr>
<td>$Z_R$</td>
<td>Racket parameter</td>
</tr>
</tbody>
</table>

**Greek:**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Attractive parameter in EOS</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Acentric factor</td>
</tr>
</tbody>
</table>
\[ \Omega_a, \Omega_b \] EOS parameters
\[ \Omega_c \] Collision integral for viscosity
\[ \Omega_D \] Collision integral for diffusion
\[ \gamma \] Activity coefficient
\[ \delta \] Stockmayer parameter
\[ \epsilon \] Molecular energy parameter \((K)\)
\[ \lambda \] Thermal conductivity \((W/m.K)\)
\[ \rho \] Molar density \( (kmol/m^3) \)
\[ \eta \] Viscosity \((Pa.s)\)
\[ \phi_i \] Fugacity coefficient of component \(i\)
\[ \phi_s \] Association factor for solvent \(s\) (Hayduk-Laudie)
\[ \psi_{ij} \] Interaction parameter for viscosities
\[ \phi_i \] Fugacity coefficient of component \(i\)
\[ \phi^* \] Pure fugacity coefficient at saturation
\[ \sigma \] Surface tension \((N/m)\)
\[ \sigma_b \] Collision diameter \((Angstrom)\)
\[ \sigma_t \] Surface tension at \(T_b \) \((N/m)\)
\[ \mu \] Dipole moment \((Debye)\)
\[ \xi \] Inverse viscosity (defined in text)

**Superscripts:**
- \(L\) Liquid
- \(V, G\) Vapour, gas
- \(*\) Saturated liquid,
  \[ T/\epsilon \]

**Subscripts:**
- \(b\) at normal boiling point
- \(c\) critical
- \(i\) of component \(i\)
- \(j\) of component \(j\)
- \(m\) mixture
- \(r\) reduced
- \(s\) saturated liquid

**Abbreviations:**
- EOS Equation of State
- RK Redlich-Kwong
- SRK Soave Redlich-Kwong
- PR Peng-Robinson
References


Chapter 3

Flash Calculations

A flash is a one stage operation where a (multiple phase) feed is "flashed" to a certain temperature and/or pressure and the resulting phases are separated. The flash in ChemSep deals only with two different phases leaving, a vapour and a liquid. Liquid-Liquid or multiphase Vapour-Liquid-Liquid flashes are currently not yet supported in ChemSep. For more information see also the general references given at the end of this chapter.

3.1 Equations

The vapour and liquid streams leaving the flash are assumed to be in equilibrium with each other. The equations that model equilibrium flashes are summarized below:

- The Total Material Balance:
  \[ V + L - F = 0 \] (3.1)

- The Component Material Balances:
  \[ V y_i + L x_i - F z_i = 0 \] (3.2)

- The Equilibrium relations:
  \[ K_i x_i - y_i = 0 \] (3.3)

- The Summation equation:
  \[ \sum_{i=1}^{c} (y_i - x_i) = 0 \] (3.4)
The heat (or enthalpy) balance:

\[ VH^v + LH^l - FH^f + Q = 0 \]

where \( F \) is the molar feedrate with component mole fractions \( z_i \). \( V \) and \( L \) are the leaving vapour and liquid flows with mole fractions \( y_i \) and \( x_i \), respectively. Equilibrium ratios \( K_i \) and enthalpies \( H \) are computed from property models as discussed in chapter 2. \( Q \) is defined as the heat added to the feed before the flash. If we count the equations listed, we will find that there are \( 2c + 3 \) equations, where \( c \) is the number of components. As flash variables we have (depending on the type of flash):

- \( c \) vapour mole fractions, \( y_i \);
- \( c \) liquid mole fractions, \( x_i \);
- vapour flowrate, \( V \);
- liquid flowrate, \( L \);
- temperature, \( T \);
- pressure, \( p \); and
- heat duty, \( Q \).

Since we have \( 2c + 3 \) equations, two of the \( 2c + 5 \) variables above need not be specified. ChemSep allows the following nine flash specifications:

- PT: pressure and temperature
- PV: pressure and vapour flow
- PL: pressure and liquid flow
- PQ: pressure and heat duty
- TV: temperature and vapour flow
- TL: temperature and liquid flow
- TQ: temperature and heat duty
- VQ: vapour flow and heat duty
- LQ: liquid flow and heat duty
3.2 Solution of the Flash Equations

FLASH uses Newton’s method for solving flash problems as well as simpler bubble and dew point calculations. The vector of variables used in the PQ-FLASH is:

\[(X)^T = (V, y_1, y_2 \ldots y_c, T, x_1, x_2 \ldots x_c, L)\]  \hspace{1cm} (3.6)

the vector of functions, \((F)\), is:

\[(F)^T = (TMB, CMB_1, CMB_2 \ldots CMB_c, H, EQM_1, EQM_2 \ldots EQM_c, SUM),\]  \hspace{1cm} (3.7)

The structure of the Jacobian matrix \([J]\) is shown below:

<table>
<thead>
<tr>
<th></th>
<th>V</th>
<th>y</th>
<th>T</th>
<th>x</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMB</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>CMB</td>
<td></td>
<td>|</td>
<td>|</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>EQM</td>
<td></td>
<td>#</td>
<td></td>
<td></td>
<td>#</td>
</tr>
<tr>
<td>SUM</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The symbols used in this diagram are as follows:

- x single matrix element
- 1 single element with a value of unity
- \| vertical column of c elements
- \ \ diagonal with c elements
- # square submatrix of order c
- - row submatrix with c elements

References


Chapter 4

Equilibrium Columns

This chapter describes the equilibrium stage model for column operations such as distillation, absorption and extraction. The equations that ChemSep solves are discussed as well as other issues.

4.1 Introduction

Multicomponent separation processes like distillation, absorption and extraction have been modelled using the equilibrium stage concept for a century. The equilibrium stage model was first used by Sorel in 1893 to describe the rectification of alcohol. Since that time it has been applied with ever increasing frequency to all manner of separation processes: distillation (including rectification, stripping, simple (single feed, two product columns), complex (multiple feed, multiple product columns), extractive, azeotropic and petroleum refinery distillation), absorption, stripping, liquid-liquid and supercritical extraction.

The equations that model equilibrium stages are called the MESH equations. The MESH equations for the interior stages of a column together with equations for the reboiler and condenser (if they are needed) are solved together with any specification equations to yield, for each stage, the vapour mole fractions; the liquid mole fractions; the stage temperature and the vapour and liquid flowrates.

Since the late 1950’s, hardly a year has gone by without the publication of at least one (and usually more than one) new algorithm for solving the equilibrium stage model equations. One of the incentives for the continued activity has always been (and remains) a desire to solve problems with which existing methods have trouble. The evolution of algorithms for solving the MESH equations has been influenced by, among other things: the availability (or lack) of sufficient computer storage and power, the development of mathematical tech-
niques that can be exploited, the complexity of physical property (K-value and enthalpy) correlations and the form of the model equations being solved.

It is not completely clear who first implemented a simultaneous correction method for solving multicomponent distillation and absorption problems. As is so often the case, it would appear that the problem was being tackled by a number of people independently. Simultaneous solution of all the MESH equations was suggested as a method of last resort by Friday and Smith (1964) in a classic paper analysing the reasons why other algorithms fail. They did not, however, implement such a technique. The two best known and most frequently cited papers are those of Goldstein and Stanfield (1970) and Naphtali and Sandholm (1971), the latter providing more details of an application of Newton’s method described by Naphtali at an AIChE meeting in May 1965.

To the best of our knowledge, a method to solve all the MESH equations for all stages at once using Newton’s method was first implemented by Whitehouse (1964) (see, also, Stainthorp and Whitehouse, 1967). Among other things, Whitehouse’s code allowed for specifications of purity, T, V, L or Q on any stage. Interlinked systems of columns and nonideal solutions could be dealt with even though no examples of the latter type were solved by Whitehouse. Since the pioneering work of Whitehouse, Naphtali and Sandholm and Goldstein and Stanfield, many others have employed Newton’s method or one of its relatives to solve the MESH equations.

Simultaneous correction procedures have shown themselves to be generally fast and reliable. Extensions to the basic method to include complex column configurations, interlinked columns, nonstandard specifications and applications to column design result in only minor changes in the algorithm. In addition, simultaneous correction procedures can easily incorporate stage efficiencies within the calculations (something that is not always possible with other algorithms). Developments to about 1980 have been described in a number of textbooks (see, for example, Holland, 1963, 1975, 1981; King, 1980; Henley and Seader, 1981) and a recent review by Wang and Wang (1980). Seader (1985) has written an interesting history of equilibrium stage simulation.

Seader (1986) lists a number of things to be taken into consideration when designing a simultaneous correction method; a revised and extended list follows and is discussed in more detail below.

1. What equations should be used?
2. What variables should be used?
3. How should the equations be ordered?
4. How should the variables be ordered?
5. How should the linearized equations be solved?
6. Should the Jacobian be updated on each iteration or should it be held constant for a number of iterations or should it be approximated using quasi-Newton methods. Should derivatives of physical properties be retained in the calculation of the jacobian (J)?

7. Should flexibility in specifications be provided and, if so, how?

8. What criterion should we use to determine convergence?

9. How should the initial guess be obtained?

10. What techniques should we use to improve reliability?

### 4.2 Equations

Each equilibrium stage in the column has a vapour entering from the stage below and liquid from a stage above. They are brought into contact on the stage together with any fresh or recycle feeds. The vapour and liquid streams leaving the stage are assumed to be in equilibrium with each other. A complete separation process is modeled as a sequence of such equilibrium stages. Each stage can have optional side draws where part of the vapour or liquid stream leaving the stage is leaving the column.

The equations that model equilibrium stages are termed the MESH equations, MESH being an acronym referring to the different types of equations that form the mathematical model. The M equations are the Material balance equations, the E equations are the Equilibrium relations, the S equations are the Summation equations and the H equations are the enthalpy balances:

- **Total Material Balance:**
  \[
  M_j^T = (W_j + V_j) + (U_j + L_j) - V_{j+1} - L_{j-1} - F_j = 0
  \]  
  (4.1)

- **Component Material Balances:**
  \[
  M_{ij} = (W_j + V_j)y_{ij} + (U_j + L_j)x_{ij} - V_{j+1}y_{i,j+1} - L_{j-1}x_{i,j-1} - F_jz_{ij}
  \]  
  (4.2)

- **Equilibrium relations:**
  \[
  E_{ij} = K_{ij}x_{ij} - y_{ij} = 0
  \]  
  (4.3)

- **Summation equations:**
  \[
  S_j^V = \sum_{i=1}^{c} y_{ij} - 1 = 0
  \]  
  (4.4)

  \[
  S_j^L = \sum_{i=1}^{c} x_{ij} - 1 = 0
  \]  
  (4.5)
Heat balance:

\[ H_j = (W_j + V_j)H_j^V + (U_j + L_j)H_j^L - V_{j+1}H_{j+1}^V - L_{j-1}H_{j-1}^L - F_jH_j^F + Q_j = 0 \] (4.6)

where we have vapour and liquid leaving flows from stage \( j \), \( V_j \) and \( L_j \), with mole fractions \( y_{ij} \) and \( x_{ij} \), vapour and liquid side-draws, \( W_j \) and \( U_j \), feeds \( F_j \) with mole fractions \( z_{ij} \), equilibrium K-values \( K_{ij} \), enthalpies \( H_j \), and stage heat duty \( Q_j \).

If we count the equations listed, we will find that there are \( 2c + 4 \) equations per stage. However, only \( 2c + 3 \) of these equations are independent. These independent equations are generally taken to be the \( c \) component mass balance equations, the \( c \) equilibrium relations, the enthalpy balance and two more equations. These two equations can be the two summation equations or the total mass balance and one of the summation equations (or an equivalent form). The \( 2c + 3 \) unknown variables determined by the equations are the \( c \) vapour mole fractions, \( y \); the \( c \) liquid mole fractions, \( x \); the stage temperature, \( T \) and the vapour and liquid flowrates, \( V \) and \( L \). For a column of \( s \) stages, we must solve \( s(2c + 3) \) equations. The table below shows how we may easily end up having to solve hundreds or even thousands of equations.

<table>
<thead>
<tr>
<th>( c )</th>
<th>( s )</th>
<th>( s(2c + 3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>650</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>690</td>
</tr>
<tr>
<td>40</td>
<td>100</td>
<td>8300</td>
</tr>
</tbody>
</table>

The first entry in this table corresponds to a simple binary problem that could easily be solved graphically. The second and third are fairly typical of the size of problem encountered in azeotropic and extractive distillation processes. The last two entries are typical of problems encountered in simulating hydrocarbon and petroleum mixture separation operations.

### 4.3 Condenser and Reboiler

The MESH equations can be applied as written to any of the interior stages of a column. In addition to these stages, the reboiler and condenser (if they are included) for the column must be considered. The MESH equations shown above may be used to model these stages exactly as you would any other stage in the column. For these special stages it is common to use some specification equation instead of the enthalpy balance. Typical specifications include:
1. the flowrate of the distillate/bottoms product stream,

2. the mole fraction of a given component in either the distillate or bottoms product stream,

3. a component flow rate in either the distillate or bottoms product stream,

4. a reflux/reboil ratio or rate,

5. the temperature of the condenser or reboiler,

6. a heat duty to the condenser or reboiler.

ChemSep includes all of these specifications as well as a few others that have not been listed.

In the case of a total condenser, the vapour phase compositions used in the calculation of the equilibrium relations and the summation equations are those that would be in equilibrium with the liquid stream that actually exists. That is for the total condenser, the vapour composition used in the equilibrium relations is the vapour composition determined during a bubble point calculation based on the actual pressure and liquid compositions found in the condenser. At the same time, these compositions are not used in the component mass balances since there is no vapour stream from a total condenser.

4.4 "Nonequilibrium" Stages

In actual operation the trays of a distillation column rarely, if ever, operate at equilibrium despite attempts to approach this condition by proper design and choice of operating conditions. The degree of separation is, in fact, determined as much by mass and energy transfer between the phases being contacted on a tray or within sections of a packed column as it is by thermodynamic equilibrium considerations. The usual way of dealing with departures from equilibrium in multistage towers is through the use of stage and/or overall efficiencies. The Murphree stage efficiency is most often used in separation process calculations because it is easily combined with the equilibrium relations:

\[ E_{ij} = E_{ij}^{MV} K_{ij} x_{ij} - y_{ij} - (1 - E_{ij}^{MV}) y_{i,j+1} = 0 \]  (4.7)

where \( E_{ij}^{MV} \) is the Murphree vapour efficiency for stage \( j \). If the efficiency is unity we obtain the original equilibrium relation from above. The Murphree efficiency must be specified for all stages except the condenser and reboiler which are assumed to operate at equilibrium.
4.5 Solution of the MESH Equations

Almost every one of the many numerical methods that have been devised for solving systems of nonlinear equations has been used to solve the MESH equations. However, as mentioned earlier, ChemSep uses mostly the Newton’s method to solve the nonlinear algebraic MESH equations. Here we will discuss how ChemSep uses the Newton’s method.

4.5.1 How to Order the Equations and Variables?

Separation problems in ChemSep result in stages with each a set of various types of equations. There are basically two ways to group the equations and variables: by type or by stage. Grouping the equations and variables by stage is preferred for problems with more stages than components (practically all distillation and many absorption and extraction problems) while grouping by type is preferred for systems with more components than stages (some gas absorption problems). ChemSep employs a by-stage grouping of the equations and variables. We define a vector of variables for the $j$-th stage as:

$$(X_j)^T = (V_j, y_{1j}, y_{2j}, \ldots, y_{cj}, x_{1j}, x_{2j}, \ldots, x_{cj}, L_j) \quad (4.8)$$

and a vector of functions for the $j$-th stage ($F_j$):

$$(F_j)^T = (M_j^T, M_{1j}, M_{2j}, \ldots, M_{cj}, H_j, E_{1j}, E_{2j}, \ldots, E_{cj}, S_j^{L-V}) \quad (4.9)$$

where

$$S_j^{L-V} = \sum_{i=1}^{c} (x_{ij} - y_{ij}) = 0 \quad (4.10)$$

If the equations and variables are grouped by stage we have

$$(F)^T = ((F_1)^T, (F_2)^T, \ldots, (F_s)^T) \quad (4.11)$$

$$(X)^T = ((X_1)^T, (X_2)^T, \ldots, (X_s)^T) \quad (4.12)$$
4.5.2 The Jacobian

To evaluate the Jacobian matrix, one must obtain the partial derivative of each function with respect to every variable. Part of the appeal of the grouping by stage approach is that for single columns at least the Jacobian matrix is block tridiagonal in structure:

\[
\begin{bmatrix}
[B_1] & [C_1] \\
[A_2] & [B_2] & [C_2] \\
& & \\
& & \\
& & \\
& & \\
[A_{m-1}] & [B_{m-1}] & [C_{m-1}] \\
[A_m] & [B_m] &
\end{bmatrix}
\]

in which each entry \([A], [B], [C]\) is a matrix in its own right. The \([A]\) submatrices contain partial derivatives of the equations for the \(j\)-th stage with respect to the variables for stage \(j-1\). The \([B]\) submatrices contain partial derivatives of the equations for the \(j\)-th stage with respect to the variables for the \(j\)-th stage. Finally, the \([C]\) submatrices contain partial derivatives of the equations for the \(j\)-th stage with respect to the variables for stage \(j+1\).

The structure of the submatrices \([A], [B] \text{ and } [C]\) is shown below.

<table>
<thead>
<tr>
<th></th>
<th>([A])</th>
<th>([B])</th>
<th>([C])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V) (y) (T) (x) (L)</td>
<td>(V) (y) (T) (x) (L)</td>
<td>(V) (y) (T) (x) (L)</td>
</tr>
<tr>
<td>TMB</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
<tr>
<td>CMB</td>
<td>(\backslash)</td>
<td>(1) (\backslash) (\backslash) (\backslash) (\backslash)</td>
<td>(1) (\backslash) (\backslash) (\backslash) (\backslash)</td>
</tr>
<tr>
<td>H</td>
<td>(x) (-) (x)</td>
<td>(x) (-) (x) (-) (x)</td>
<td>(x) (-) (x)</td>
</tr>
<tr>
<td>EQM</td>
<td>#</td>
<td>#</td>
<td>#</td>
</tr>
<tr>
<td>SUM</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The symbols used in these diagrams are as follows:

- \(x\) single matrix element
- \(1\) single element with a value of unity
- \(\backslash\) vertical column of \(c\) elements
- \(\backslash\) diagonal with \(c\) elements
- \(#\) square submatrix of order \(c\)
- \(-\) row submatrix with \(c\) elements
The elements of \([B]\) include partial derivatives of \(K\)-values with respect to temperature and composition. Since it is rather a painful experience to differentiate, for example, the UNIQUAC equations with respect to temperature and composition, in some SC codes this differentiation is done numerically. This can be an extremely time consuming step. However, neglect of these derivatives is not recommended unless one is dealing with nearly ideal solutions, since, to do so, will almost certainly lead to an increase in the required number of iterations or even to failure.

Almost all of the partial derivatives needed in \texttt{ChemSep} are computed from analytical expressions. The exception is the temperature derivatives of the excess enthalpy which requires a second differentiation with respect to temperature of the activity and fugacity coefficient models. Coding just the first derivatives was bad enough.

If the column has pumparounds extra matrices will be present which are not on the diagonal and the use of block tridiagonal methods becomes less straightforward. Similar problems arise with non-standard specifications that are not on the variables of the condenser and reboiler. When we solve multiple interconnected columns (currently not supported by \texttt{ChemSep}) a special ordering is required to maintain the diagonal structure of the jacobian. Therefore, \texttt{ChemSep} now uses a sparse solver to solve the system of equations involved.

### 4.5.3 How Should the Linearized Equations be Solved?

It is absolutely essential to take account of the sparsity of the Jacobian when solving the linearized equations; straightforward matrix inversion is totally impractical (and probably numerically impossible). Linear systems with a block tridiagonal structure may reasonably efficiently be solved using a generalized form of the Thomas algorithm. The steps of this algorithm are given by Henley and Seader (1981).

Still further improvements in the block elimination algorithm for solution of separation process problems can be effected if we take advantage of the special structure of the submatrices \([A]\), \([B]\) and \([C]\). In fact, \([A]\) and \([C]\) are nearly empty. \texttt{ChemSep} uses the sparse matrix solver \texttt{NSPIV} for solving the sparse linear system effectively.

### 4.5.4 The Initial Guess

In order to obtain convergence, Newton’s method requires that reasonable initial estimates be provided for all \(s(2c + 3)\) independent variables. \texttt{ChemSep} uses an automatic initialization procedure where the user does not need to make any guesses. Flow rates are estimated assuming constant molar flows from stage to stage. If the bottoms flow rate and reflux ratio are NOT specified and cannot be estimated from the specifications that are supplied then the bottoms flow rate is arbitrarily assigned a value of half the total feed flow and the
reflux ratio is given a default value of 2. This, of course, could cause serious convergence problems. In the future, *optional guesses* might be added to the specifications to circumvent this problem.

The next step is to estimate the compositions and temperatures. This is done iteratively. We start by estimating the K-values assuming ideal solution behavior at the column average pressure and an estimate of the boiling point of the combined feeds. (This eliminates the normal requirement of estimates of end stage temperatures).

Mole fractions of both phases are estimated by solving the material balance and equilibrium equations for one component at a time.

We define a column matrix of discrepancy functions

\[
(F)^T = (M E_{i,1}^c, \ldots M E_{i,j}^c, \ldots M E_{i,s}^c)
\]

where \(M E_{ij}^c\) is the component material balance equation combined with the equilibrium equations to eliminate the vapour phase mole fractions. Each equation depends on only three mole fractions. Thus, if we define a column matrix of mole fractions \((X)\) by

\[
(X)^T = (x_{i,1}, \ldots x_{i,j-1}, x_{ij}, x_{i,j+1}, x_{i,s})
\]

we may write

\[
(F) = [A B C] (X) - (R) = (0)
\]

With the equations and variables ordered in this way, the coefficient matrix \([A B C]\) has *three* adjacent diagonals with coefficients:

\[
A_j = L_{j-1}
\]

\[
B_j = -(V_j K_{ij} + L_j)
\]

\[
C_j = V_j K_{ij}
\]

The right hand side matrix \((R)\) has elements

\[
R_j = -F_j z_{ij}
\]

This linear system of equations can be solved for the mole fractions very easily using Gaussian elimination. Temperatures and vapour compositions are computed from a bubble point calculation for each stage. The bubble point computation provides K-values for all components on all stages. So we solve the tridiagonal system of equations again using the old flow rates and the new K-values. Temperatures are recomputed as before. This procedure is repeated a third time before proceeding with the main simulation.

For columns without condenser and reboiler a different initialization is used where the compositions of the liquid are set equal to the top liquid feed compositions and the compositions of the vapour equal to the bottom vapour feed compositions. Temperatures in the whole column are set equal to the temperature of the first feed specified.
For columns with either a condenser or a reboiler the compositions are initialized to the overall compositions of all feeds combined, and the temperatures to the bubble point at the column pressure and the overall feed compositions.

Currently there is no special initialization routine that will handle pumparound if they are present. The result is that columns with large pumparound flows will require flow initialization by the user, or, to repetitively solve the problem using the old results as the initialization and increasing pumparound flow (see below).

### 4.5.5 Reliability

SC methods are far more reliable and versatile than most other methods. The same method will solve distillation, gas absorption and liquid extraction problems. It must be admitted though, that although the probability that Newton's method will converge from the automatic initial estimates is quite high, there is no guarantee of convergence. The difficulty of supplying good initial estimates is particularly severe for problems involving strongly nonideal mixtures, interlinked systems of columns and nonstandard specifications.

Several methods have been used to improve the reliability of Newton's method; damping the Newton step, use of steepest descent (ascent) formulations for some of the iterations, and combination with relaxation procedures; none of which has proven to be completely satisfactory. The methods most recently proposed for assisting convergence of Newton's method are continuation methods.

In default mode, ChemSep does NOT use any of these techniques, other than a check to make sure that all quantities remain positive. Mole fractions, for example, are not permitted to take on negative values. The user does have the option of supplying damping factors.

### 4.5.6 Damping factors

The Newton's method in ChemSep has some extra features that will enhance the convergence to the solution. The Newton's method computes a new solution vector based on the current Jacobian and function vector. However, the new solution vector might be physically meaningless, for example if a composition becomes smaller than zero or larger than unity. Also, the new solution vector might represent too large a change in stage temperatures or flows for the method to be stable. To alleviate these problems ChemSep uses damping of the newton's iteration changes. Temperature changes are limited to a maximum (default to 10 K) and flow changes up to a maximum fraction of the old flows (default set to 0.5).

The compositions require a special type of damping. If a composition is becoming negative or larger than unity, the change is limited to half the distance to the extreme. Also, if a damping factor is specified, the maximum change in composition equals the factor (the de-
fault factor is 1 allowing a change over the whole mol fraction range). This type of damping has turned out to be very effective. The damping factors can be found under the Options - Solve options menu.

If for some reason your column simulation does not converge, changing the damping factors might help. If you know the iteration history (by either limiting the number of iterations or by printing out the intermediate answers. Both can be done in the Options - Solve options menu) you can adapt the factors so the column simulation might converge. Note that convergence is mostly slower when you start to apply extra damping by making the factors smaller, the Newton method looses its effectiveness when damped. Nor does damping guarantee convergence.

4.5.7 User Initialization

For difficult problems it might be necessary for the user to provide initial temperature, pressure, or flow profiles. In case the stage temperatures or pressures are not calculated user initialization is a way to define these profiles.

The user can specify either temperature or flow profiles, or both. The only requirement is that values for the first and last stages are provided. Missing temperatures on intermediate stages are computed by linear interpolation, missing flows are computed on a constant flow from stage to stage basis. Therefore, it is better to specify the flows of the first and last two stages in case a condenser and reboiler are present. Composition profiles are computed through the method described above, however, temperatures are not computed using the bubble point calculations. If both user specified temperature and flow profiles are incomplete ChemSep switches to the automatic initialization method.

4.5.8 Initialization with Old Results

In some cases it might prove advantageous to use the converged results of a previous run as the initial guess for a new problem (for example, when bottoms flowrate and reflux rate are not specified and cannot be estimated, and the automatic initialization always uses a reflux ratio of 2). This is a very straightforward way of specifying the initial guess as long as the number of components remains the same. Care must be taken when feed or product specifications or locations are changed. The results are interpolated if the number of stages is changed.
References


J.C. Wang, Y.L. Wang, "A Review on the Modeling and Simulation of Multi-Stage Sep-


Chapter 5

Nonequilibrium Columns

The nonequilibrium model and the model equations are introduced. Models that describe the mass transfer, the flow type, pressure drop, entrainment, and weeping are discussed. The design method which enables the simultaneous design of the the column layout and column simulation is explained.

5.1 The Nonequilibrium Model

A second generation nonequilibrium model was developed by Taylor and coworkers and is described in detail by Taylor et al. (1994) and Taylor and Krishna (1993). It can be used to simulate trayed columns as well as packed columns. Packed columns are simulated with stages representing a discrete integration over the packed bed. The more stages are used the better the integration, and the more accurate the results will be (to check if the specified number of stages in a packed column simulation was sufficient, increase the number of stages and repeat the column simulation, the results should be similar). A schematic diagram of a nonequilibrium stage is shown in Figure 5.1. This stage may represent one (or more than one) tray in a trayed column or a section of packing in a packed column. The vertical wavy line in the middle of the diagram represents the interface between the two phases which may be vapor and liquid (distillation), gas and liquid (absorption) or two liquids (extraction).

Figure 5.1 also serves to introduce the notation used in writing down the equations that model the behavior of this nonequilibrium stage. The flow rates of vapor and liquid phases leaving the $j$-th stage are denoted by $V_j$ and $L_j$ respectively. The mole fractions in these streams are $y_{ij}$ and $x_{ij}$. The $N_{ij}$ are the molar fluxes of species $i$ on stage $j$. When multiplied by the area available for interphase mass transfer we obtain the rates of interphase mass transfer. The temperatures of the vapor and liquid phases are not assumed to be equal and we must allow for heat transfer as well as mass transfer across the interface.
Figure 5.1: Schematic diagram of a nonequilibrium stage (after Taylor and Krishna, 1993).
If Figure 5.1 represents a single tray then the term $\phi_j^V$ is the fractional liquid entrainment defined as the ratio of the moles of liquid entrained in the vapor phase in stage $j$ to the moles of downflowing liquid from stage $j$. Similarly, $\phi_j^L$ is the ratio of vapor entrained in the liquid leaving stage $j$ (carried down to the tray below under the downcomer) to the interstage vapor flow. For packed columns, this term represents axial dispersion. Weeping in tray columns may be accounted for with a similar term.

The component material balance equations for each phase may be written as follows:

$$M_{ij}^V \equiv (1 + r_j^V + \phi_j^V)V_j y_{ij} - V_{j+1} y_{i,j+1} - \phi_{j-1}^V V_{j-1} y_{i,j-1} - f^V_{ij} - \sum_{\nu=1}^{n} G_{ij \nu}^V + N_{ij}$$

$$= 0 \quad i = 1, 2, \ldots, c$$

(5.1)

$$M_{ij}^L \equiv (1 + r_j^L + \phi_j^L)L_j x_{ij} - L_{j-1} x_{i,j-1} - \phi_{j+1}^L L_{j+1} x_{i,j+1} - f^L_{ij} - \sum_{\nu=1}^{n} G_{ij \nu}^L - N_{ij}$$

$$= 0 \quad i = 1, 2, \ldots, c$$

(5.2)

where $G_{ij \nu}$ is the interlinked flow rate for component $i$ from stage $\nu$ to stage $j$, and $n$ is the number of total stages (trays or sections of packing). The last terms in Equations (5.1) and (5.2) are the mass transfer rates (in kmol/s), where mass transfer from the “V” phase to the “L” phase is defined as positive. At the V/L interface we have continuity of mass and, thus, the mass transfer rates in both phases must be equal.

The total material balances for the two phases are obtained by summing Equations (5.1) and (5.2) over the component index $i$.

$$M_{ij}^V \equiv (1 + r_j^V + \phi_j^V)V_j - V_{j+1} - \phi_{j-1}^V V_{j-1} - F_j^V - \sum_{i=1}^{c} \sum_{\nu=1}^{n} G_{ij \nu}^V + N_{ij}$$

$$= 0$$

(5.3)

$$M_{ij}^L \equiv (1 + r_j^L + \phi_j^L)L_j - L_{j-1} - \phi_{j+1}^L L_{j+1} - F_j^L - \sum_{i=1}^{c} \sum_{\nu=1}^{n} G_{ij \nu}^L - N_{ij}$$

$$= 0$$

(5.4)

$F_j$ denotes the total feed flow rate for stage $j$, $F_j = \sum_{i=1}^{c} f_{ij}$.

Here total flow rates and mole fractions are used as independent variables and total as well as component material balances are included in the set of independent model equations. In the nonequilibrium model of Krishnamurthy and Taylor (1985a) component flow rates were treated as variables.

The nonequilibrium model uses two sets of rate equations for each stage:

$$R_{ij}^V \equiv N_{ij} - N_{ij}^V = 0 \quad i = 1, 2, \ldots, c - 1$$

(5.5)

$$R_{ij}^L \equiv N_{ij} - N_{ij}^L = 0 \quad i = 1, 2, \ldots, c - 1$$

(5.6)
where $N_{ij}$ is the mass transfer rate of component $i$ on stage $j$. The mass transfer rate in each phase is computed from a diffusive and a convective contribution with

$$N_{ij}^V = a_{ij}^V J_{ij}^V + y_{ij} N_{ij}$$

$$N_{ij}^L = a_{ij}^L J_{ij}^L + x_{ij} N_{ij}$$

where $a_{ij}^V$ is the total interfacial area for stage $j$ and $N_{ij}^V$ is the total rate on stage $j$ ($N_{ij} = \sum_{i=1}^c N_{ij}$). The diffusion fluxes $J$ are given by (in matrix form):

$$J^V = c^V [k^V (y^V - y)]$$

$$J^L = c^L [k^L (x^L - x)]$$

where $(y^V - y^L)$ and $(x^L - x^L)$ are the average mole fraction difference between the bulk and the interface mole fractions (Note that the fluxes are multiplied by the interfacial area to obtain mass transfer rates). How the average mole fraction differences are calculated depends on the selected flow model. The matrices of mass transfer coefficients, $[k]$, are calculated from

$$[k^P] = [R^P]^{-1} [\Gamma^P]$$

where $[\Gamma^P]$ is a matrix of thermodynamic factors for phase $P$. For systems where an activity coefficient model is used for the phase equilibrium properties the thermodynamic factor matrix $\Gamma$ (order $c - 1$) is defined by

$$\Gamma_{ij} = \delta_{ij} + x_i \left( \frac{\partial \ln \gamma_i}{\partial x_j} \right)_{T,P,x_k,k \neq j = 1..c-1}$$

If an equation of state is used $\gamma_i$ is replaced by $\phi_i$. Expressions for the composition derivatives of $\ln \gamma_i$ are given by Taylor and Kooijman (1991). The rate matrix $[R]$ (order $c - 1$) is a matrix of mass transfer resistances calculated from the following formulae:

$$R_{ii}^P = \frac{z_i}{k_{i}^P} + \sum_{k=1,k \neq i}^{c} \frac{z_k}{k_{ik}^P}$$

$$R_{ij}^P = -z_i \left( \frac{1}{k_{ij}^P} - \frac{1}{k_{ic}^P} \right)$$

where $k_{ij}^P$ are binary pair mass transfer coefficients for phase $P$. Mass transfer coefficients, $k_{ij}$, are computed from empirical models (Taylor and Krishna, 1993) and multicomponent diffusion coefficients evaluated from an interpolation formula (Kooijman and Taylor, 1991). Equations (5.13) and (5.14) are suggested by the Maxwell-Stefan equations that describe mass transfer in multicomponent systems (see Taylor and Krishna, 1993). The matrix of thermodynamic factors appears because the fundamental driving force for mass transfer is the chemical potential gradient and not the mole fraction or concentration gradient. This matrix is calculated from an appropriate thermodynamic model. The binary mass transfer coefficients are estimated from empirical correlations as functions of column internal type as well as design, operational parameters, and physical properties including the binary pair
Maxwell-Stefan diffusion coefficients. Thus, the mass transfer coefficient models form the basis of the nonequilibrium model and it is possible to change the behavior of a column by selecting a different mass transfer coefficient correlation.

Note that there are $c$ times $c$ binary pair Maxwell-Stefan diffusion coefficients, but only $c - 1$ times $c - 1$ elements in the $[R^F]$ and $[k^F]$ matrices and, therefore, only $c - 1$ equations per set of rate equations. This is the result of the fact that diffusion calculations only yield relative transfer rates. We will need an extra equation that will "bootstrap" the mass transfer rates: the energy balance for the interface. Note also that in this model the flux correction on the mass transfer coefficients has been neglected.

The energy balance equations on stage $j$ are written for each phase as follows:

$$E_j^V \equiv (1 + r_j^V + \phi_j^V)V_j H_j^V - V_{j+1} H_{j+1}^V - \phi_{j-1}^V V_{j-1} H_{j-1}^V - F_j^V H_j^{VF} - \sum_{\nu=1}^{n} G_{j\nu}^V H_{j\nu}^V + Q_j^V + e_j^V = 0 \quad (5.15)$$

$$E_j^L \equiv (1 + r_j^L + \phi_j^L)L_j H_j^L - L_{j-1} H_{j-1}^L - \phi_{j+1}^L L_{j+1} H_{j+1}^L - F_j^L H_j^{LF} - \sum_{\nu=1}^{n} G_{j\nu}^L H_{j\nu}^L + Q_j^L - e_j^L = 0 \quad (5.16)$$

where $G_{j\nu}$ is the interlink flow rate from stage $\nu$ to stage $j$. The last term in the left-hand-side of Equations (5.15) and (5.16), $e_j$, represents the energy transfer rates for the vapor and liquid phase which are defined by

$$e_j^V = a_j^V h^V (T_V - T_I) + \sum_{i=1}^{c} N_{ij}^V \bar{H}_{ij}^V \quad (5.17)$$

$$e_j^L = a_j^L h^L (T_I - T_L) + \sum_{i=1}^{c} N_{ij}^L \bar{H}_{ij}^L \quad (5.18)$$

where $\bar{H}_{ij}$ are the partial molar enthalpies of component $i$ for stage $j$. We also have continuity of the energy fluxes across the V/L interface which gives the interface energy balance:

$$E_j^I \equiv e_j^V - e_j^L = 0 \quad (5.19)$$

where $h^V$ and $h^L$ are the vapor and liquid heat transfer coefficients respectively, and $T^V$, $T^I$, and $T^L$ the vapour, interface, and liquid temperatures. For the calculation of the vapor heat transfer coefficients the Chilton-Colburn analogy between mass and heat transfer is used:

$$Le = \frac{\lambda}{DC_p} = \frac{Sc}{Pr} \quad (5.20)$$

$$h^V = k\rho C_p Le^{2/3} \quad (5.21)$$
For the calculation of the liquid heat transfer coefficients a penetration model is used:

\[ h^L = k \rho C_p \sqrt{Le} \]  \hspace{1cm} (5.22)

where \( k \) is the average mass transfer coefficient and \( D \) the average diffusion coefficient.

In the nonequilibrium model of Krishnamurti and Taylor (1985a) the pressure was taken to be specified on all stages. However, column pressure drop is a function of tray (or packing) type and design and column operating conditions, information that is required for or available during the solution of the nonequilibrium model equations. It was, therefore, quite straightforward to add an **hydraulic** equation to the set of independent equations for each stage and to make the pressure of each stage (tray or packed section) an unknown variable. The stage is assumed to be at mechanical equilibrium so \( p_j^V = p_j^L = p_j \).

In the second generation model, the pressure of the top tray (or top of the packing) is specified along with the pressure of any condenser. The pressure of trays (or packed sections) below the topmost are calculated from the pressure of the stage above and the pressure drop on that tray (or over that packed section). If the column has a condenser (which is numbered as stage 1 here) the hydraulic equations are expressed as follows:

\[ P_1 \equiv p_c - p_1 = 0 \]  \hspace{1cm} (5.23)

\[ P_2 \equiv p_{spec} - p_2 = 0 \]  \hspace{1cm} (5.24)

\[ P_j \equiv p_j - p_{j-1} - (\Delta p_{j-1}) = 0 \quad j = 3, 4, \ldots, n \]  \hspace{1cm} (5.25)

where \( p_c \) is the specified condenser pressure, \( p_{spec} \) is the specified pressure of the tray or section of packing at the top of the column, and \( \Delta p_{j-1} \) is the pressure drop per tray or section of packing from section/stage \( j-1 \) to section/stage \( j \). If the top stage is not a condenser, the hydraulic equations are expressed as

\[ P_1 \equiv p_{spec} - p_1 = 0 \]  \hspace{1cm} (5.26)

\[ P_j \equiv p_j - p_{j-1} - (\Delta p_{j-1}) = 0 \quad j = 2, 3, \ldots, n \]  \hspace{1cm} (5.27)

In general we may consider the pressure drop to be a function of the internal flows, the fluid densities, and equipment design parameters.

\[ \Delta p_{j-1} = f(V_{j-1}, L_{j-1}, \rho_{j-1}^V, \rho_{j-1}^L, Design) \]  \hspace{1cm} (5.28)

The pressure drop term, \( \Delta p_{j-1} \), is calculated from liquid heights on the tray (from various correlations, see Lockett, 1986, and Kister, 1992) or specific pressure drop correlations for packings (see the section below on pressur drop models).

For bubble cap trays the procedures described by Bolles (1963) can be adapted for computer based calculation. Kister (1992) also covers methods available for estimating the pressure
Table 5.1: Nonequilibrium model equations type and number

<table>
<thead>
<tr>
<th>Equation</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material balances</td>
<td>2c + 2</td>
</tr>
<tr>
<td>Energy balances</td>
<td>3</td>
</tr>
<tr>
<td>transfer Rate equations</td>
<td>2c − 2</td>
</tr>
<tr>
<td>Summations equations</td>
<td>2</td>
</tr>
<tr>
<td>Hydraulic equation</td>
<td>1</td>
</tr>
<tr>
<td>interface equilibrium relations</td>
<td>c</td>
</tr>
<tr>
<td>Total MERSHQ</td>
<td>5c + 6</td>
</tr>
</tbody>
</table>

The pressure drop in structured packed columns may be estimated using the method of Bravo et al. (1986).

Phase equilibrium is assumed to exist only at the interface with the mole fractions in both phases related by:

\[ Q_{ij}^I = K_{ij}^I x_{ij} - y_{ij}^I = 0 \quad i = 1, 2, \ldots, c \]  (5.29)

where \( K_{ij} \) is the equilibrium ratio for component \( i \) on stage \( j \). The \( K_{ij} \) are evaluated at the (calculated) temperature, pressure, and mole fractions at the interface.

The mole fractions must sum to unity in each phase:

\[ S_j^Y = \sum_{i=1}^{c} y_{ij} - 1 = 0 \]  (5.30)

\[ S_j^L = \sum_{i=1}^{c} x_{ij} - 1 = 0 \]  (5.31)

as well as at the interface:

\[ S_{jI}^Y = \sum_{i=1}^{c} y_{ij}^I - 1 = 0 \]  (5.32)

\[ S_{jI}^L = \sum_{i=1}^{c} x_{ij}^I - 1 = 0 \]  (5.33)

Table 5.1 lists the type and number of equations for the nonequilibrium model. To solve the model we have \( 5c + 6 \) equations and variables, where \( c \) is the number of components. They are solved simultaneously using Newton’s method.

Nonequilibrium and equilibrium models require similar specifications. Feed flows and their thermal condition must be specified for both models, as must the column configuration (number of stages, feed and sidestream locations etc.). Additional specifications that are the same for both simulation models include the specification of, for example, reflux ratios or bottom product flow rates if the column is equipped with a condenser and/or a reboiler. The
Table 5.2: Currently supported column internals for the nonequilibrium model

<table>
<thead>
<tr>
<th>Bubble-cap trays</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieve trays</td>
</tr>
<tr>
<td>Valve trays (including double weight valves)</td>
</tr>
<tr>
<td>Dumped packings</td>
</tr>
<tr>
<td>Structured packings</td>
</tr>
<tr>
<td>Equilibrium stage (with Murphree stage efficiency)</td>
</tr>
<tr>
<td>Rotating Disk Contactor (RDC) compartment (for extraction)</td>
</tr>
</tbody>
</table>

specification of the pressure on each stage is necessary if the pressure drop is not computed; if it is, only the top stage pressure needs be specified (the pressure of all other stages being determined from the pressure drop equations that are part of the model described above).

If we solve the nonequilibrium model with Newton’s method, we also require initial guesses for all the variables. ChemSep uses the same automatic initial guess routine for the nonequilibrium model as the equilibrium model. The temperatures of the vapour, interface, and liquid are initialized all equal to the temperature from the automatic guess. Mass and energy transfer rates are initialized as zero and the interface mole fractions are set equal to the bulk mole fractions which are also provided by the initial guess. Pressure drops are initially assumed to be zero.

The nonequilibrium model, in comparison with the equilibrium model, requires the evaluation of many more physical properties and of the heat and mass transfer coefficients. In addition, a nonequilibrium simulation cannot proceed without some knowledge of the column type and the internals layout. Tray type and mechanical layout data, for example, is needed in order to calculate the mass transfer coefficients for each tray. For packed columns the packing type, size and material must be known. Libraries with standard tray and packing data are available on-line. Table 5.2 lists the currently supported types of column internals.

To avoid the problem that during the design of a column no column layout is available, the nonequilibrium column simulator has an optional design mode to automatically assign layout parameters. The user just needs to select one of the types of internals (for each section in the column). The design-mode is activated by not specifying the column diameter (leaving it as a "default" with "*") for a specific section. With the design-mode "on" each tray or stage is automatically adapted during each iteration while keeping the layout within each section the same.

For the evaluation of the heat and mass transfer coefficients, pressure drop, and the entrainment/weeping flows a nonequilibrium simulation needs the following:
Table 5.3: Available mass transfer coefficient correlations per internals type

<table>
<thead>
<tr>
<th>Bubble-Cap tray</th>
<th>Sieve tray</th>
<th>Valve tray</th>
<th>Dumped packing</th>
<th>Structured packing</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIChE Hughmark</td>
<td>AIChE</td>
<td>AIChE</td>
<td>Onda 68</td>
<td>Bravo 85</td>
</tr>
<tr>
<td>Chan-Fair</td>
<td>Zuidersweg</td>
<td>Harris</td>
<td>Bravo 82</td>
<td>Bravo 92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bubble-Jet</td>
<td>Billet 92</td>
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<td></td>
<td></td>
<td></td>
<td>Billet 92</td>
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</tbody>
</table>

- Mass transfer coefficient model
- Column internals type
- Column internals layout or design mode parameters (such as fraction of flooding etc.)
- Flow model for both phases
- Entrainment and weeping models
- Pressure drop model

Each of these are discussed in separate sections below.

5.2 Mass Transfer Coefficient Correlations

Mass transfer models are the basis of the nonequilibrium model. The models incorporated in ChemSep are all from the published literature. It is possible to change the behavior of a column by selecting a different mass transfer correlation. Therefore, we have tried to document the origin of the data of each method in order to guide you in selecting models. Table 5.3 gives a summary of the available correlations per type of internals. The various correlations are discussed below.

Binary mass transfer coefficients (MTC’s) can be computed from Number of Transfer Units (NTU’s = N) by:

\[ k^V = \frac{N^V}{t_V a^V} \]  \hspace{2cm} (5.34)

\[ k^L = \frac{N^L}{t_L a^L} \]  \hspace{2cm} (5.35)

where the vapor and liquid areas are calculated with

\[ a^V = \frac{a_d}{ch_f} \]  \hspace{2cm} (5.36)

\[ a^L = \frac{a_d}{ch_f} \]  \hspace{2cm} (5.37)
the interfacial area density is computed according Zuiderweg (1982).

5.2.1 Trays

**AIChE** Correlates the number of transfer units for sieve and bubble-cap trays:

\[
N^V = (0.776 + 4.57h_w - 0.238F_s + 104.8Q_L/W_i)/\sqrt{Sc_V} \tag{5.38}
\]

\[
F_s = u_s/\sqrt{\rho_l^V} \tag{5.39}
\]

\[
Sc_V = \mu^V/\rho_l^V D^V \tag{5.40}
\]

\[
N^L = 19700/\sqrt{D_l}(0.4F_s + 0.17)t_L \tag{5.41}
\]

\[
t_L = h_L Z/\rho L \tag{5.42}
\]

The clear liquid height \( h_L \) is computed from Bennett et al. (1983):

\[
h_L = \alpha e \left( h_w + C(Q_L/\alpha e W_i)^{0.67} \right) \tag{5.43}
\]

\[
\alpha e = \exp(-12.55(u_s/(\rho^V/(\rho_l^L - \rho^V))^{0.5})^{0.91}) \tag{5.44}
\]

\[
C = 0.50 + 0.438 \exp(-137.8h_w) \tag{5.45}
\]

**Chan-Fair** The vapor number of transfer units is:

\[
N^V = (10300 - 8670F_f)F_f/\sqrt{D^V}t_V/\sqrt{h_L} \tag{5.46}
\]

\[
t_V = (1 - \alpha e)h_L/(\alpha e u_s) \tag{5.47}
\]

For the liquid number of transfer units the same correlations as given for the AIChE method is used \((h_L \text{ and } \alpha e \text{ are also computed with the correlation of Bennett et al.})\).

**Zuiderweg** The vapor phase mass transfer coefficient is

\[
k^V = 0.13/\rho_l^V - 0.065/(\rho_l^V)^2 \tag{5.48}
\]

in which \( k^V \) becomes independent of the diffusion coefficient. The liquid mass transfer coefficient is computed from either:

\[
k^L = 2.6 \times 10^{-5}(\mu^L)^{-0.25} \tag{5.49}
\]

or

\[
k^L = 0.024(D^L)^{0.25} \tag{5.50}
\]

The interfacial area is computed in the spray regime from:

\[
a_d h_f = \frac{40}{\phi^{0.37}} \left( \frac{U_l^2 \rho_l^V h_L F P}{\sigma} \right)^{0.37} \tag{5.51}
\]
or in the froth-emulsion regime:

\[ a_d h_f = \frac{43}{\phi^{0.3}} \left( \frac{U_s^2 \rho_V h_L F_P}{\sigma} \right)^{0.37} \]  

(5.52)

The transition from the spray to mixed froth-emulsion flow is described by:

\[ F_P > 3bh_L \]  

(5.53)

where \( b \) is the weir length per unit bubbling area:

\[ b = W_i/A_b \]  

(5.54)

and the clear liquid height is given by:

\[ h_L = 0.6h_w^{0.5} (pF_P/b)^{0.25} \]  

(5.55)

**Hughmark** The numbers of transfer units are given by:

\[ N^V = (0.051 + 0.0105F_s) \sqrt{\frac{p_L}{F_s}} \]  

(5.56)

\[ N^L = (-44 + 10.7747 \times 10^4 Q/L/W_i + 127.1457F_s) \sqrt{D_L A_{pib}/Q_L} \]  

(5.57)

**Harris** The numbers of transfer units are given by:

\[ N^V = \frac{0.3 + 15t_G}{\sqrt{Sc_G}} \]  

(5.58)

\[ N^L = \frac{5 + 10t_L(1 + 0.17(0.82F_s - 1)(39.3h_w + 2))}{\sqrt{Sc_L}} \]  

(5.59)

**Chen-Chuang** The numbers of transfer units for the vapour is:

\[ t_V = \frac{h_i}{u_s} \]  

(5.60)

\[ F_s = U_s \sqrt{\rho_V} \]  

(5.61)

\[ N^V = 11 \frac{1}{\eta_L^{0.1/3.0.14}} \left( \frac{\rho_L F_s^2}{\sigma^2} \right)^{1/3} \sqrt{D_V t_V} \]  

(5.62)

and for the liquid

\[ t_L = \frac{\rho_L}{\rho_V} t_V \]  

(5.63)

\[ N^L = 14 \frac{1}{\eta_L^{0.1/3.0.14}} \left( \frac{\rho_L F_s^2}{\sigma^2} \right)^{1/3} \left( \frac{V}{L} \right) \sqrt{D_L t_L} \]  

(5.64)
This is a fundamental model of tray performance where mass transfer calculations are split over several zones (see Taylor and Krishna, 1993). The jetting-bubble formation region, the free bubbling zone, and the splash zone. The mass transfer in the splash zone is neglected and parameters for the bubble and jet zones need to be supplied by the user. A bi-modal bubble distribution is assumed and the mass transfer coefficient is obtained from theoretical relations. The plug-flow model is used for describing the mass transfer from the vapour side. The following parameters are input:

1. Height of the jetting zone, \( h_j \) (m)
2. Diameter of the jets, \( d_j \) (m)
3. Vapour velocity in the jet, \( u_j \) (m/s)
4. Height of the free bubbling zone, \( h_b \) (m)
5. Small bubble diameter, \( d_s \) (m)
6. Small bubble rise velocity, \( u_s \) (m/s)
7. Small bubble volume fraction, \( f_s \) (-)
8. Big bubble diameter, \( d_b \) (m)
9. Big bubble rise velocity, \( u_b \) (m/s)
10. Big bubble volume fraction, \( f_b \) (-)

These parameters are not all independent, for example, the volume fraction of small and big bubble must sum to unity. If one of the input parameters is missing (or, if both \( h_j \) and \( h_b \) are zero) we can compute all of the parameters according to correlations obtained from Prado (1986):

\[
d_s = 1.36d_h^{0.9857} 
\]

\[
u_s = \sqrt{\frac{(2.14\sigma + 0.505\rho_f g d_s^2)}{\rho_f d_s}} 
\]

\[
d_b = 0.8868d_h^{0.8464} u_h^{0.21} 
\]

\[u_b = \frac{u_v}{(1 - f_s)(1 - h_{cl}/h_f)} - \frac{u_s f_s}{(1 - f_s)} \]

\[
f_s = 165.65d_h^{1.32} \beta^{1.33} 
\]

\[
f_b = 1 - f_s 
\]

\[
h_b = h_f - h_j 
\]

\[
\beta = \frac{A_h}{A_{bab}} 
\]

\[
h_j = 2.853 \times 10^{-6} Re_h 
\]

\[Re_h = \frac{d_j u_h \rho}{\eta} \]

\[
d_j = 1.1d_h + 0.25h_{cl} 
\]

\[u_j = \frac{u_h d^2_j}{(1 - FLC)d^2_j} \]
where parameters as $h_f$ and $h_{cl}$ can be computed by empirical correlations for the tray (here sieve tray since the correlations were obtained with that particular tray type). The fraction of inactive holes, $FLC$, can be set to zero or estimated by

$$FLC = 1836.97u_h^{-1.002}Q_L^{0.524}h_w^{0.292}$$  \hspace{1cm} (5.77)

Currently this model is not available in ChemSep.

5.2.2 Random Packings

OTO-68 Onda et al. (1968) [parameters $a_p$, $d_p$, $\sigma_c$] developed correlations of mass transfer coefficients for gas absorption, desorption, and vaporization in random packings. The vapor phase mass transfer coefficient is obtained from

$$k^V = ARe_1^{0.7}Sc_1^{0.333}(a_pD^V(a_p d_p))^{-2}$$  \hspace{1cm} (5.78)

where $A = 2$ if $d_p < 0.012$ and $A = 5.23$ otherwise. Vapour and liquid velocities are calculated by

$$u_V = VM^V/\rho^V A_t$$  \hspace{1cm} (5.79)
$$u_L = LM^L/\rho^LA_t$$  \hspace{1cm} (5.80)

and Reynolds and Schmidt numbers:

$$Re_V = \frac{\rho^V u_V}{(\eta^V a_p)}$$  \hspace{1cm} (5.81)
$$Re_L = \frac{\rho^L u_L}{(\eta^L a_p)}$$  \hspace{1cm} (5.82)
$$Sc_V = \frac{\eta^V}{(\rho^V D^V)}$$  \hspace{1cm} (5.83)
$$Sc_L = \frac{\eta^L}{(\rho^L D^L)}$$  \hspace{1cm} (5.84)

The liquid phase mass transfer coefficient is

$$k^L = 0.0051(Re_L^{1.2/3}Sc_L^{-0.5}(a_p d_p)^{0.4}(\eta^L g/\rho^L)^{1/3})$$  \hspace{1cm} (5.85)

where $Re_L^I$ is the liquid Reynolds number based on the interfacial area density

$$Re_L^I = \frac{\rho^L u_L}{(\eta^I a_d)}$$  \hspace{1cm} (5.86)

The interfacial area density, $a_d (m^2/m^3)$, is computed from

$$a_d = a_p \left[1 - \exp \left(-1.45(\sigma_c/\sigma)^{0.75}Re_L^{0.1}Fr_L^{-0.05}We_L^{0.2}\right)\right]$$  \hspace{1cm} (5.87)
where

\[ Fr_L = \frac{a_p u_L^2}{g} \]  
\[ We_L = \frac{\rho_L u_L^2}{a_p \sigma} \]

\( BF-82 \) Bravo and Fair (1982) [parameters \( a_p, d_p, \sigma_c \)] used the correlations of Onda et al. for the estimation of mass transfer coefficients for distillation in random packings by using an alternative relation for the interfacial area density:

\[ a_d = 19.78 (Ca_L Re_V)^{0.392} \sqrt{\sigma} H^{-0.4} a_p \]

where \( H \) is the height of the packed section and \( Ca_l \) is the capillary number

\[ Ca_L = u_L \eta^L / \rho^L \sigma \]

Since the interfacial area density is used in the calculation for the liquid Reynolds number the Bravo and Fair method will result in different mass transfer coefficients.

\( BS-92 \) Billet and Schultes (1992) [parameters \( a_p, \epsilon, C_{fl}, C_h, C_p, C_v, C_l \)] describe an advanced empirical/theoretical model which is dependent on the pressure drop/holdup calculation (\( C_h, C_p, C_{fl} \)). The correlation can be used for both random and structured packings. Vapour and liquid phase resistance are fitted each by parameter (\( C_v \) and \( C_l \)), bringing the total number of parameters to five. There are trends in the parameters that can be observed from tabulated data. Unfortunately, no such generalization was done by Billet, making use of the model dependent on the availability of the parameters or experimental data. The mass transfer coefficients are computed by

\[ k^L = C_l \left( \frac{g \rho_L}{\eta_L} \right)^{1/6} \sqrt{\frac{DL}{d_h}} \left( \frac{u_L}{a_p} \right)^{1/3} \]

\[ k^V = C_v \left( \frac{1}{\sqrt{\epsilon - h_L}} \right) \sqrt{\frac{a}{d_h}} D^V (Re_V)^{3/4} (Sc_V)^{1/3} \]

where Reynolds and Schmidt numbers are calculated as in Onda et al. The hydraulic diameter \( d_h \) is

\[ d_h = 4\epsilon / a_p \]

and the liquid holdup fraction, \( h_L \), is calculated as described below under the pressure drop section. The interfacial area density is given by:

\[ a_d = a_p (1.5 / \sqrt{a_p d_h}) (u_L d_h \rho^L / \eta^L)^{-0.2} (u_L^2 \rho^L d_h / \sigma)^{0.75} (u_L^2 / gd_h)^{-0.45} \]
5.2.3 Structured packings

BRF-85 Bravo et al. (1985) [parameters $a_p$, $\epsilon$, $B$, $h_c$, $S$, $D_{eq}$, $\theta$] published correlations for structured packings. This method is based on the assumption that the surface is completely wetted and that the interfacial area density is equal to the specific packing surface: $a_d = a_p$. The Sherwood number for the vapour phase is

$$Sh_V = 0.0338 Re_V^{0.8} Sc_V^{0.333}$$

(5.96)

and is defined by

$$Sh_V = \frac{k^V d_{eq}}{D^V}$$

(5.97)

The equivalent diameter of a channel is given by

$$d_{eq} = B h_c [1/(B + 2S) + 1/2S]$$

(5.98)

where $B$ is the base of the triangle (channel base), $S$ is the corrugation spacing (channel side), and $h_c$ is the height of the triangle (crimp height). The vapour phase Reynolds number is defined by

$$Re_V = \frac{d_{eq} \rho^V (u_{Ve}\text{eff} + u_{Le}\text{eff})}{\eta^V}$$

(5.99)

The effective velocity of vapour through the channel, $u_{Ve}$, is

$$u_{Ve}\text{eff} = u_V / (\epsilon \sin \theta)$$

(5.100)

($u_V$ is the superficial vapour velocity, $\epsilon$ the void fraction, and $\theta$ the angle of the channel with respect to the horizontal). The effective velocity of the liquid is

$$u_{Le}\text{eff} = \frac{3\Gamma}{2\rho L} \left( \frac{(\rho L)^2 g}{3\eta L \Gamma} \right)^{1/3}$$

(5.101)

where $\Gamma$ is the liquid flow rate per unit of perimeter

$$\Gamma = \rho^L u_L / P$$

(5.102)

where $P$ is the perimeter per unit cross-sectional area, computed from

$$P = (4S + B) / Bh_c$$

(5.103)

The penetration model is used to predict the liquid phase mass transfer coefficients with the exposure time assumed to be the time required for the liquid to flow between corrugations (a distance equal to the channel side):

$$t_L = S / u_{Le}\text{eff}$$

(5.104)

$$k^L = 2 \sqrt{\frac{D^L}{\pi t_L}}$$

(5.105)
Nawrocki et al. (1991) [parameter \( P \)] developed a combination of a theoretical model for the liquid distribution in structured packing and the empirical correlation of Bravo et al. (1985) for the mass transfer coefficients. It is capable of predicting the mass transfer coefficients in small-distributed columns. Unfortunately, values of the model parameter \( P \) are unknown for any packing and must be evaluated from experimental data. *Currently this model is not available in ChemSep.*

Bravo et al. (1992) [parameters \( a_p, \epsilon, S, \theta, F_{se}, K_2, C_e, dPdz_{flood} \)] developed a theoretical model for modern structured packings. Four parameters can be supplied, however, the authors advise a fixed value for the surface renewal correction \((C_e)\), normally 0.9. They provide a relation for parameter \( K_2 \) as well:

\[
K_2 = 0.614 + 71.35S \quad (5.106)
\]

The mass transfer calculations are dependent on the pressure drop/holdup calculations. The effective area can be adjusted with the surface enhancement factor \( F_{se} \), and the liquid resistance with a correction on the surface renewal following the penetration model (parameter \( C_e \)). Effective velocities are computed with

\[
u_{L,\text{eff}} = \frac{u_L}{\epsilon} h_t \sin \theta \quad (5.107)
\]

\[
u_{G,\text{eff}} = \frac{u_V}{\epsilon (1 - h_t)} \sin \theta \quad (5.108)
\]

where \( h_t \) is the fractional liquid holdup (see below at the section on pressure drop calculation). Reynolds numbers and liquid mass transfer coefficient is now calculated as in Bravo et al. (1985) but with

\[
t_L = C_e S / \nu_{L,\text{eff}} \quad (5.109)
\]

However, the vapour phase mass transfer coefficient is obtained from

\[
k^V = 0.054 \left( \frac{D_V}{S} \right) R e_V^{0.8} S c_V^{1/3} \quad (5.110)
\]

where the equivalent diameter is replaced with the channel side \( S \) and a different coefficient is used. The assumption of a completely wetted packing is dropped, the interfacial area density is given by

\[
a_d = F_t F_{se} a_p \quad (5.111)
\]

\[
F_t = \frac{29.12 (W e_L F r_L)^{0.35} S^{0.359}}{R e_L^{0.2} \epsilon^{0.6} (\sin \theta)^{0.3} (1 - 0.93 \cos \gamma)} \quad (5.112)
\]

where \( \cos \gamma \) is equal to 0.9 for \( \sigma < 0.0453 \), otherwise it is computed by

\[
\cos \gamma = 5.211 \times 10^{-16} \times 835 \sigma \quad (5.113)
\]

Note that a different switch point is used than reported by Bravo et al. (1992) to guarantee continuity in \( \cos \gamma \).

Billet and Schultes (1992) [parameters \( a_p, \epsilon, C_I, C_h, C_p, C_v, C_l \)] developed a model for both random and structured packings, see the section on random packings above.
5.3 Flow Models

For the calculation of the diffusion fluxes the average mole fraction difference between the bulk and the interface mole fractions were required (see Equations 5.9 and 5.10). How these average mole fraction differences are computed depends on the selected flow model. Here three flow models are discussed: mixed flow, plug flow, and dispersion flow (which is only applied to the liquid phase).

5.3.1 Mixed flow

If we assume both phases are present in a completely mixed state, we can use

\[
\begin{align*}
(y^V - y^I) &= (y^V - y^I) \\
(x^I - x^L) &= (x^I - x^L)
\end{align*}
\]

(5.114)  (5.115)

this keeps the rate equations (relatively) simple and only a function of the mole fractions leaving the current stage. However, on a tray where the vapour bubbles through a liquid which flows from one downcomer to the opposite downcomer this model is not accurate. Indeed, only for very small diameter columns will the mixed flow model give reasonable results. The mixed model is the most simple flow model and is the easiest to converge. For packed columns the convergence to the true column profiles by using increasing number of stages can be quite slow using the mixed flow model.

5.3.2 Plug flow

In the plug-flow model we assume that the vapour or liquid moves in plug flow (thus, without mixing) through the froth. This complicates the rate equations so much that no exact solution is possible. The mass transfer actually needs to be integrated over the froth. To approximate the total mass transfer an average mole fraction difference is computed. Kooijman and Taylor (1994) derived expressions for the average vapour and liquid compositions assuming constant mass transfer coefficients and that the interface compositions is constant (it isn’t, but its “average” value is obtained):

\[
\begin{align*}
(y^V - y^I) &= \Omega[-N^V](y^V - y^I) \\
(x^I - x^L) &= \Omega[-N^L](x^I - x^L)
\end{align*}
\]

(5.116)  (5.117)

where the mole fractions are of the leaving streams and the number of mass transfer units (N) for the vapour and liquid are defined as:

\[
\begin{align*}
N^V &= c_I^V k^V a^V h_f A_b / V \\
N^L &= c_I^L k^L a^L h_f A_b / L
\end{align*}
\]

(5.118)  (5.119)
and $\Omega[M]$ is a matrix function defined as

$$\Omega[M] = [\exp[M] - [I]][M]^{-1}[\exp[M]]^{-1} = [\exp[-M] - [I]][-M]^{-1}$$

(5.120)

Using this model predicted efficiencies for tray column experiments can be more accurately described. The plug flow model can also be used for packed columns, providing a much faster convergence to the true column profiles compared to the mixed flow model.

Currently no correction terms is applied to the plug flow model to correct for the change in mole fractions over the integration (as is discussed by Kooijman and Taylor, 1994).

5.3.3 Dispersion flow

In the dispersion-flow model we assume the liquid to flow over the tray in plug flow with dispersion. Kooijman and Taylor (1994) also derived a formula to compute the average mole fraction difference for the liquid phase for this case. However, it is rather involved:

$$(x^L - x^F) = [p][\exp[m] - [I]][m]^{-1}[\exp[m]]^{-1} - [m][\exp[p] - [I]][p]^{-1}[\exp[p]]^{-1} \left[ b^{-1} \frac{(X_{out})}{2} \right]$$

(5.121)

where we have defined

$$a = Pe/2 = \frac{LZ}{Dc Whc e_L}$$

(5.122)

$$[b] = a[2[N^L/b + [I]]^{1/2}$$

(5.123)

$$[p] = a[I] + [b]$$

(5.124)

$$[m] = a[I] - [b]$$

(5.125)

Currently only a binary implementation is working for the dispersion model. Eddy dispersion coefficient are computed from Zuiderweg's (1982) correlation (this model is recommended by Korchinsky, 1994).

Results of the dispersion flow model are close to the plug flow model. How close depends on the eddy dispersion coefficient. Expect that the dispersion coefficient is larger for smaller diameter columns and trays with small weirs (or low liquid heights). We intend to extend the number of correlations predicting this coefficient. For now, it is advised to not use this flow model and it is not available.

5.4 Pressure Drop Models

Nowadays, there are many models and ways to compute tray pressure drops. For packings we see a shift from generalized pressure drop charts (GPDC) to more theoretically based
correlations. We have chosen to employ the most recently published models. For packings we have 7 methods available (see Table 5.4). For packing operating above the loading point ($FF > 0.7$) we advise the use of models that take the correction for the liquid holdup into account, such as SBF-89, BS-92, and BRF-92. BRF-92 has the advantage of requiring very few fitted parameters, but is limited to structured packings.

Pressure drop can also be fixed to the pressure at the top of the section. However, this will can have an important effect on the designed column diameter, especially at very low pressures.

### 5.4.1 Tray pressure drop estimation

The liquid heights on the trays are evaluated from the tray pressure drop calculations. The wet tray pressure drop liquid height is calculated with:

$$h_{wt} = h_d + h_l$$  \hspace{1cm} (5.126)

where $h_d$ is the dry tray pressure drop liquid height and $h_l$ the liquid height:

$$h_l = h_{cl} + h_r + \frac{h_{lg}}{2}$$  \hspace{1cm} (5.127)

The clear liquid height, $h_{cl}$, is calculated with

$$h_{cl} = \alpha h_w + h_{ow}$$  \hspace{1cm} (5.128)

where the liquid fraction $\alpha$ is computed with the Barker and Self (1962) correlation:

$$\alpha = \frac{0.37h_w + 0.012F_s + 1.78Q_L/W_t + 0.024}{1.06h_w + 0.035F_s + 4.82Q_L/W_t + 0.035}$$  \hspace{1cm} (5.129)

The choice of correlation for the liquid fraction turns out to be important as certain correlations are dynamically unstable. The height of liquid over the weir, $h_{ow}$, is computed by

<table>
<thead>
<tr>
<th>Bubble-Cap tray</th>
<th>Sieve tray</th>
<th>Valve tray</th>
<th>Dumped packing</th>
<th>Structured packing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
</tr>
<tr>
<td>Estimated</td>
<td>Estimated</td>
<td>Estimated</td>
<td>Ludwig 79</td>
<td>Billet 92</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Leva 92</td>
<td>Bravo 86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Billet 92</td>
<td>Stichlmair 89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bravo 92</td>
</tr>
</tbody>
</table>
various correlations for different types of weirs (see Perry) and a weir factor \( F_w \) correction (see Smith, pp. 487) is employed. For example for a segmental weir:

\[
\begin{align*}
    h_{aw} &= 0.664 F_w \left( \frac{Q_w}{W_t} \right)^{2/3} \\
    w &= \frac{W_t}{D_c} \\
    F_w^3 &= \frac{w^2}{1 - (F_w w (1.08 Q_L)^{2/3} + \sqrt{1 - w^2})^2}
\end{align*}
\]

where \( Q_L \) is the volumetric flow over the weir per weir length. The residual height, \( h_r \), is only taken into account for sieve trays. Bennett’s method (see Lockett, pp. 81) is:

\[
    h_r = \left( \frac{6}{1.27 \rho_L} \right) \left( \frac{\sigma}{g} \right)^{2/3} \left( \frac{\rho_L - \rho_V}{d_h} \right)^{1/3}
\]

Dry tray pressure, \( h_d \), is calculated with:

\[
    h_d = K_{DG} \frac{\rho_L}{\rho_c} u_h^2
\]

\[
    K = \frac{\xi}{2g}
\]

where the orifice coefficient \( \xi \) for sieve trays is computed according to Stichlmair and Mersmann (1978). For valve trays we use the method of Klein (1982) as described in Kister (1992, pp. 309–312) where \( K \) is given for the cases with the valves closed or open. It is extended for double weight valve trays as discussed by Lockett (1986, pp. 82–86). The dry tray pressure drop is corrected for liquid fractional entrainment.

The froth density is computed with

\[
    h_f = \frac{h_{cl}}{\alpha}
\]

The liquid gradient, \( h_{lg} \), is computed according to Fair (Lockett, 1986, pp. 72):

\[
    R_h = \frac{W h_f}{W + 2h_f}
\]

\[
    U_f = \frac{Q_L}{W h_{cl}}
\]

\[
    Re_f = \frac{R_h U_f \rho_L}{\eta_L}
\]

\[
    f = 7 \times 10^4 h_w R e_f^{1.06}
\]

\[
    h_{lg} = \frac{Z f U_f^2}{g R_h}
\]

where \( W \) is the average flow-path width for liquid flow, and \( Z \) the flow path length. The height of liquid at the tray inlet is:

\[
    h_i = \sqrt{\frac{2}{g} \left( \frac{Q_L}{W_t} \right)^2 \left( \frac{1}{h_{cl}} - \frac{1}{h_c} \right) + \frac{2 \alpha h_f^2}{3}}
\]
where \( h_c \) is the height of the clearance under the downcomer. The pressure loss under downcomer (expressed as a liquid height) is

\[
h_{udc} = \left( \frac{1}{2g} \right) \left( \frac{Q_L}{C_d W h_c} \right)^2
\]

(5.143)

where \( C_d = 0.56 \) according to Koch design rules. The height of liquid in the downcomer can now be calculated with the summation:

\[
h_{db} = h_{wt} + h_i + h_{udc}
\]

(5.144)

Bubble-cap liquid heights are done according to Perry’s (1984) and Smith (1963). Additionally the liquid fraction of the froth is computed according to Kastanek (1970).

### 5.4.2 Random packing pressure drop correlations

For packings the vapour and liquid mass flow per cross sectional area \((kg/m^2s)\) and velocities \((m/s)\) are:

\[
L_a = LM^L/A_t
\]

(5.145)

\[
V_a = VM^V/A_t
\]

(5.146)

\[
u_L = L_a/\rho^L
\]

(5.147)

\[
u_V = V_a/\rho^V
\]

(5.148)

**Lud-79** Ludwig (1979) [parameters \(A, B\)] supplied a simple empirical equation for the pressure drop requiring two fitted parameters (see Wankat, 1988, 420–428):

\[
\frac{\Delta p}{\Delta z} = 3.281 \times 10^2 \left( \frac{0.2048 V_a}{0.06243 \rho V} \right)^2 10^{B(0.06243L_a)}
\]

(5.149)

where 3.281 242, 0.2048, and 0.06243 are conversion factors so that we can use A and B parameters from Wankat. Its accuracy is limited since the influence of physical properties as viscosity or surface tension on A and B are not included. Even more, the fitted parameters can be flow regime dependent. The loading regime is not well described with the simple exponent term.

**Lev-92** Leva (1992) [parameter \(F_p\)] devised a modified version of the Generalized Pressure Drop Correlation (GPDC), originally derived by Leva (1953). The GPDC has been the standard design method for decades. Some modifications that were actually simplifications made the GPDC lose its popularity. The function worked back from the GPDC and limiting \((L_a = 0)\) behavior is (in SI units):

\[
\frac{\Delta p}{\Delta z} = 22.3F_p (\eta^L)^{0.2} \phi V_a^2 \frac{10^{0.035L_a}}{g \rho V}
\]

(5.150)
with \( \phi = \rho_{\text{water}}/\rho_l = 1000/\rho_l \). This result is similar to the Ludwig (1979) equation with corrections for the influence of the liquid density and viscosity. The only parameter is the packing factor \( F_p \) which can be obtained from dry pressure drop experiments (see Leva, 1992) or computed by the specific packing area over the void fraction cubed.

Again, the loading regime is not well described with the simple exponent term. This is model is the default pressure drop model for random packings if no model is specified, since it requires only the packing factor.

\[ \Delta p = 0.75 f_0 (1 - \epsilon_p) \rho^V \cdot u_V^2/(d_p \epsilon_p^{4.65}) \]  

with the void fraction of the irrigated bed, equivalent packing diameter, Reynolds number, and friction factor for a single particle are:

\[ \epsilon_p = \epsilon - h_t \]  
\[ d_p = 6(1 - \epsilon_p)a_p \]  
\[ Re_V = u_V d_p \rho^V/\eta^V \]  
\[ f_0 = C_1/Re_V + C_2/\sqrt{Re_V} + C_3 \]

Iteration is started by assuming a dry bed for which \( \epsilon_p = \epsilon \) and the holdup fraction is computed with the liquid Froude number:

\[ Fr_L = u_L^2 a_p/\rho \epsilon^{4.65} \]  
\[ h_t = 0.555 Fr_L^{1/3} \]

The liquid holdup is limited to 0.5 in order to handle flooding.

\[ BS-92 \] Billet and Schultes (1992) and Billet’s monograph (1979?) [parameters \( a, \epsilon, C_l, C_h, C_p \)] include an extensive model and an extensive lists of packing data with fitted parameters. The method is rather complicated but has two regimes. The method does correct for the holdup change in the loading regime but employs an empirical exponential term, and is not iterative.

Packing dimension, hydraulic diameter and F-factor are

\[ d_p = 6(1 - \epsilon)/a_p \]  
\[ d_h = 4\epsilon/a_p \]  
\[ F_s = u_V \sqrt{\rho^V} \]
Liquid Reynolds and Froude number are

\[ Re_L = \frac{u_L \rho_L \eta^2 a_p}{\eta^2 a_p} \]  \hspace{1cm} (5.161)
\[ Fr_L = \frac{u_L^2 a_p}{g} \]  \hspace{1cm} (5.162)

If \( Re_L < 5 \) then

\[ aha = C_h Re_L^{0.15} Fr_L^{0.1} \]  \hspace{1cm} (5.163)

else

\[ aha = 0.85 C_h Re_L^{0.25} Fr_L^{0.1} \]  \hspace{1cm} (5.164)

\[ h1 = \left( \frac{12 \eta^2 a_p^2 u_L}{\rho L g} \right)^{1/3} \]  \hspace{1cm} (5.165)
\[ h2 = h1 aha^{2/3} \]  \hspace{1cm} (5.166)
\[ h_{l,fl} = 0.374 \epsilon \left( \frac{\eta^2 \rho w}{\eta w \rho L} \right)^{0.05} \]  \hspace{1cm} (5.167)

\[ \epsilon_{fl} = \left( \frac{u_L}{u_V} \right)^{0.2} \]  \hspace{1cm} (5.168)
\[ \epsilon_{fl} = g / (C_f^2 \epsilon_{fl}^{0.39}) \]  \hspace{1cm} (5.169)
\[ u_{w,fl} = \left( \frac{2g}{\epsilon_{fl} (\epsilon - h_{l,fl})} \right)^{1.5} \left( \frac{h_{l,fl}}{a_p \sqrt{\rho_L / \rho V}} \right) \sqrt{\epsilon} \]  \hspace{1cm} (5.170)

if \( u_V > u_{w,fl} \) then \( h_t = h_{l,fl} \) else

\[ h_t = h2 + (h_{l,fl} - h2) (u_V / u_{w,fl})^{1.3} \]  \hspace{1cm} (5.171)

The pressure drop is then

\[ K_1 = 1 + (2/3)(1/1 - \epsilon)(d_p / D_c) \]  \hspace{1cm} (5.172)
\[ Re_V = u_V d_p \rho V / (1 - \epsilon) \eta V K_1 \]  \hspace{1cm} (5.173)
\[ \phi_{l1} = C_p (64 / Re_V + 1.8 / Re_V^{0.08}) \exp(Re_L / 200)(h_t / h1)^{0.3} \]  \hspace{1cm} (5.174)
\[ \frac{\Delta p}{\Delta z} = \phi_{l1} (a_p / (\epsilon - h1)^{1.3}) (R_s^2 / 2) K_1 \]  \hspace{1cm} (5.175)

5.4.3 Structured packing pressure drop correlations

BRF-86 Bravo et al. [parameters \( \epsilon, S, \sin(\theta), C_3 \)] compute the pressure drop from an empirical correlation with one fitted parameter, called \( C_3 \). This model is unsuitable for pressure
drop correlations in the loading regime \((FF > 0.7)\). The pressure drop per height of packing is:

\[
\frac{\Delta p}{\Delta z} = (0.171 + 92.7/R_e V)(\rho V^2 u_{V,eff}/d_{eq})(\frac{1}{(1 - C_3 V F r)^5})
\]  
(5.176)

where

\[
u_{V,eff} = \frac{u_V}{(\epsilon \sin \theta)}
\]  
(5.177)

\[
R_e V = \frac{d_{eq} V u_{V,eff}}{\eta V}
\]  
(5.178)

\[
F r_L = \frac{u^2_L}{d_{eq} \eta}
\]  
(5.179)

**SBF-92** Stichlmair et al. (1989) [parameters \(a, \epsilon, C_1, C_2, C_3\)] published a semi-empirical method, see the section on pressure drop of random packed columns above.

**BRF-92** Bravo et al. (1992) [parameters \(a_p, \epsilon, S, \theta, K_2, dPd_z_{flood}\)] developed a theoretical model developed for modern structured packings. Two parameters need to be supplied for pressure drop calculations, however, the \(K_2\) parameter was fitted by the authors. The pressure of flooding \((dPd_z_{flood})\) can be easily obtained from data or via Kister’s correlation and the packing factor. The model includes an iterative method with a dependence of the liquid holdup on the pressure drop (and vice versa). The Weber, Froude, and Reynolds numbers are

\[
W e_L = \frac{u^2_L \rho L S}{\sigma}
\]  
(5.180)

\[
F r_L = \frac{u^2_L}{(S g)}
\]  
(5.181)

\[
R e_L = \frac{u_L S \rho L}{\eta L}
\]  
(5.182)

The effective \(g\) (as a function of \(h_t\)) is calculated:

\[
ge_{eff} = \left(1 - \frac{dPdZ}{dPdZ_{flood}}\right) \left(\frac{\rho L - \rho V}{\rho L}\right) g
\]  
(5.183)

Then \(F_t\) (see above), \(h_t\), and \(dPdZ\) are computed

\[
h_t = \left(\frac{4 F_t}{S}\right)^{2/3} \left(\frac{3 \eta L u_L}{\rho V \sin \theta g_{eff}}\right)^{1/3}
\]  
(5.184)

\[
A = \frac{0.177 \rho V}{S \epsilon^2 \sin(\theta)^2}
\]  
(5.185)

\[
B = \frac{88.74 \eta V}{S^2 \epsilon \sin \theta}
\]  
(5.186)

\[
\frac{\Delta p}{\Delta z} = (A u^2_V + B u_V) \left(\frac{1}{1 - K_2 h_t}\right)^5
\]  
(5.187)

The calculation is repeated until pressure drop converges or when it becomes larger than the pressure drop at flood. The iteration can actually have problems in converging.
5.5 Entrainment and Weeping

Entrainment and weeping flows (for trays only) change the internal liquid flows and influence the performance of the column internals. **ChemSep currently does not support the handling of these flows.** This is due to the fact that few entrainment models behave properly. Neither is the effect of the entrainment and weepflows on the mass transfer properly taken into account.

Entrainment is computed from the fractional liquid entrainment which is computed from Hunt’s correlation and from figure 5.11 of Lockett (1986) for sieve trays:

\[ \phi^L = 7.75 \times 10^{-5} \left( \frac{0.073}{\sigma} \right) M_v \left( \frac{U_v}{T_s - 2.5 h_{cl}} \right)^{3.2} \] \hspace{1cm} (5.188)

The weeping factor is estimated from a figure from Smith (1963, plot on page 548), which was fitted with the following correlation

\[ WF = \frac{0.135 \phi \ln(34(H_w + H_{ow}) + 1)}{(H_d + H_r)} \] \hspace{1cm} (5.189)

where \( \phi \) is the open area ratio.

5.6 The Design Mode

The initial layout is determined after the flows are known from the initial guess. Each stage in the column is designed separately and independently of adjacent stages. Then the sections in the column are rationalized so that trays or stages within a section have the same layout. During each iteration (that is, an update of the flows) each stage is re-designed only if the flowrates have changed more than by a certain fraction (which can be specified). Only sections with re-designed trays or stages are rationalized again. After convergence a complete design of any trayed or packed section in the column is obtained. In this manner trayed and packed sections can be freely mixed in a column simulation/design.

Different design methods can be employed:

- Fraction of flooding this is the standard design method for trays, we have employed a modified version of the method published by Barnicki and Davis (1989).
- Pressure drop; this is the usual design method for packed columns, but is very useful as well for tray design with pressure drop constraints.

- Optimizing; a ‘new’ way of designing columns that incorporates the different design considerations in a more rigorous manner than conventional design algorithms. It is more computationally intensive than the other two methods and only applicable for tray sections.

The methods generate a column-design that might not be optimal from an engineer’s viewpoint. They must be seen as starting points for the actual design layouts. Also, the design does not include constructional calculations to determine tray support constructions or thicknesses of trays or the column. Design mode is automatically triggered if the column diameter is not specified. Other layout parameters can be specified but they may be changed by the design mode. Each of these methods behaves differently and they are discussed in more detail below. An additional and very important de-rating factor is the system factor (SF). It represents the uncertainty in design correlations with regard to phenomena which are currently still not properly modeled, such as foaming.

Tray layout parameters that specify a complete design (for the calculation of mass transfer coefficients and pressure drops) are shown in Table 5. For packings only the column diameter and bed height are design parameters, other parameters are fixed with the selection of the type of packing (such as void fraction, nominal packing diameter, etc.). The packed bed height must be specified since it determines the desired separation and the capacity.

5.6.1 Tray Design: Fraction of flooding

The first task in this approach to tray design is to assign all layout parameters to consistent values corresponding to the required capacity defined by the fraction of flooding and current flowrates. These defaults function as starting points for subsequent designs.

The initial free area ratio is taken to be 15% of the active area. The active area is determined with capacity factor calculation with internals specific methods (for sieve and bubble-cap trays the default is Fair’s correlation by Ogboja and Kuye (19), and the Glitsch method for valve trays). The tray spacing is initially set to the default value (of 0.5m) and the downcomer area is calculated according the Glitsch manual (limited by a minimum time residence check). From the combined areas the column diameter is computed. The number of liquid passes on a tray is initially set by the column diameter; under 5ft one pass, under 8ft two, 10ft three, under 13ft four, else five passes. With the number of passes and the column diameter the total weir length is computed. Once the weir length is determined the liquid weir load is checked, if too high the number of passes is incremented and a new weir length is evaluated until the weir load is below a specified maximum.
### Table 5.5: Tray layout data

<table>
<thead>
<tr>
<th>General (sieve) tray layout data:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Column diameter</td>
<td>Active area</td>
</tr>
<tr>
<td>Number of flow passes</td>
<td>Total hole area</td>
</tr>
<tr>
<td>Tray spacing</td>
<td>Downcomer area</td>
</tr>
<tr>
<td>Liquid flow path length</td>
<td>Weir length</td>
</tr>
<tr>
<td>Hole diameter</td>
<td>Weir height</td>
</tr>
<tr>
<td>Hole pitch</td>
<td>Deck thickness</td>
</tr>
<tr>
<td>Downcomer clearance</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Additional data for bubble caps:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cap diameter</td>
<td>Slot area</td>
</tr>
<tr>
<td>Slot height</td>
<td>Riser area</td>
</tr>
<tr>
<td>Skirt clearance</td>
<td>Annual area</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Additional data for valves:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Closed Loss K</td>
<td>Open Loss K</td>
</tr>
<tr>
<td>Eddy Loss C</td>
<td>Ratio Valve Legs</td>
</tr>
<tr>
<td>Valve Density</td>
<td>Valve Thickness</td>
</tr>
<tr>
<td>Fraction Heavy Valves</td>
<td>Heavy Valve Thickness</td>
</tr>
</tbody>
</table>

Initial weir height is taken as 2”, but limited to a maximum of 15% of the tray spacing. For notched or serrated weirs the notch depth is a third of the weir height. For serrated weirs the angle of serration is 45 degrees. Circular weirs have diameters 0.9 times the weir length. Hole diameter is set to 3/16” for sieve trays and tray thickness 0.43 times the hole diameter (or 1/10”). The hole pitch is computed from the free area ratio and hole diameter according to a triangular pitch. The default downcomer clearance is 1.5” but is limited by the maximum allowed downcomer velocity according to the Glitch method de-rated with the system factor. The clearance is set to be at least half an inch lower than the weir height to maintain a positive liquid seal but is limited to a minimum of half an inch.

For bubble-cap trays the cap diameter is 3” for column diameters below 4.5 ft and 4” for above. The hole diameter can vary between 60% to 71% of the capdiameter, and default taken as 70%. Default skirt clearance is 1” with minimum of 0.5” and maximum of 1.5”. Slot height can vary in between 0.5” and 1.5”, default 1” for cap diameters below 3.5” and 1.25” for larger cap diameters. The pitch can vary from 1.25” to half the flow path length (minimum number of rows is two), default set to 1.25”.

Valve trays are initialized to be Venturi orifice uncaged, carbon steel valves of 3 mm thick with 3 legs (see Kister, 1992, p312). The hole diameter is 1” for column smaller than 4.5 ft, otherwise 2”. No double weight valves are present.
The second task in the fraction of flooding method consists of finding the proper free area ratio \( \beta = A_h/A_b = \text{hole area/active area} \) so that no weeping occurs. This ratio can vary between a minimum of 5\% (for stable operation) and a maximum of 20\%. To test whether weeping occurs, we use the correlation by Lockett and Banik (1984): \( \text{Fr}_{h,\text{weep}} > 2/3 \).

The method requires all liquid heights to be evaluated at weep rate conditions. This task is ignored for bubble-cap trays. The weep test is done at weeping conditions, with a weep factor at 60\% (this can be changed). Calculating liquid heights is done by adding various contributions with correlations from Lockett (1986) and Kister (1992), see Appendix A. If weeping occurs at the lower bound for the free area ratio, a flag is set for the final task to adapt the design.

The final task consists of evaluating all liquid heights at normal conditions and to do a number of checks:

- vapor distribution (for bubble-caps),
- weeping (for sieve/valve trays),
- hydraulic flooding,
- excessive liquid entrainment,
- froth height limit, and
- excessive pressure drop

If a check fails the design is adapted to correct the problem, according to the adjustments shown in Table 5.6 after which new areas are calculated with capacity correlations. Part of this task is also to keep the layout parameters that are adjusted within certain lower and upper bounds to maintain a proper tray design. Finally the number of iterations for the design method is checked against a maximum (default 30) to prevent a continuous loop.

The adjustment factors \( f_1, f_2, \) and \( f_3 \) are percentage decreases, normally set at 5, 2, and 1\%. These factors — together with all the default, lower, and upper settings that are used in the design routine — are stored in a “design file” (TDESIGN.DEF) that can be tailored to handle specific kinds of designs and columns. This allows the selection of different methods for capacity and hydrodynamic calculations as well. Also the fraction that the flows need to change before a re-design is issued can be changed in this manner together with other design criteria. The design file must be in the current directory for the nonequilibrium program to use it, otherwise the normal defaults will be used.

Here we discuss the most important parameters of the file. The file starts with a comment on the first line. The second line specifies the factors \( f_1, f_2, \) and \( f_3 \) for adapting the design layout parameters. The third line specifies the fraction of change allowed in the flows before a redesign occurs. It also specifies the fraction of deviation allowed in downcomer
### Table 5.6: Tray design checks and adjustments

<table>
<thead>
<tr>
<th>Problem</th>
<th>Test</th>
<th>Adjustments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble cap vapor distribution</td>
<td>$h_{lb}/h_d &gt; 0.5$</td>
<td>$p + f_1,$ $h_{skirt} + f_2,$ $h_{tot} + f_3,$ $d_h - f_3$</td>
</tr>
<tr>
<td>Weeping</td>
<td>Fr$_h/(2/3) &lt; 1 - f_a$ free &lt; 0.05</td>
<td>$A_b = A_{bf}$ $W_f + f_1$ $A_b - f_1$ $d_h - f_3$ $h_w - f_3$ $t_v + f_2 (vt)$</td>
</tr>
<tr>
<td>Hydrodynamic (downcomer) flooding</td>
<td>$T_s &lt; h_{db}/FF$</td>
<td>$T_s + f_1$ $A_b + f_1$ $T_s + f_1$ $h_w + f_2$ $h_c + f_3$</td>
</tr>
<tr>
<td>Excessive liquid entrainment</td>
<td></td>
<td>$A_b + f_1$ $T_s + f_2$ $d_h - f_2$ $h_w - f_3$</td>
</tr>
<tr>
<td>Froth height limit</td>
<td>$h_f &gt; 0.75T_s$</td>
<td>$A_b + f_1$ $T_s + f_2$ $h_w - f_3$</td>
</tr>
<tr>
<td>Excessive pressure drop</td>
<td>$gph_{wt} &gt; \Delta p_{max}$</td>
<td>$A_b + f_1$ $h_w - f_1$ $d_h + f_2$ $p + f_1 (bc)$ $h_{skirt} + f_2 (bc)$ $h_{tot} + f_3 (bc)$</td>
</tr>
<tr>
<td>Excessive vapor entrainment</td>
<td></td>
<td>$A_d + f_1$</td>
</tr>
</tbody>
</table>
and bubbling area between current and design values. Line 11 specifies the volumetric weir load after which the number of passes is incremented. Line 14 specifies the maximum froth height as fraction of the tray spacing as is used in the froth height limit check. Line 15 specifies the criterion to which the free area ratio has to converge. Line 16 sets the maximum allowed pressure drop for the excessive pressure drop check. Line 20 specifies the maximum number of loops for the design method. Line 21-23 specify the methods to calculate capacity factors for bubble-cap, sieve, and valve trays. Line 24-25 set the downcomer area method and velocity check. Line 45 sets a flag to generate tray parameter output and line 46 sets a flag for intermediate design messages.

5.6.2 Packing Design: Fraction of flooding

For packed columns only the column diameter is a design parameter to be evaluated. Default packing data are used for all packing parameters that are not specified; values of 1" inch metal Pall rings for random packed sections and of Koch Flexipack 2 (316ss) for structured sections.

To determine the packed column diameter, the diameter that gives rise to the flooding pressure drop (as specified) is computed using the selected pressure drop model. The resulting diameter is corrected for the fraction of flooding and the system factor:

\[ D_c = \frac{D_{c,\text{flood}}}{\sqrt{FF SF}} \]  

(5.190)

This does make the resulting column diameter depend on the selected pressure drop model. If no pressure drop model is selected the Leva (1992) model is selected (which is only a function of the packing factor). If no pressure drop at flood is specified, it is estimated with Kister's correlation (1992) (which is only a function of the packing factor). Thus, as long as the packing factor is known, this method will not fail.

5.6.3 Pressure drop

Tray design on pressure drop works as discussed above but with a default fraction of flooding of 75%. However, the specified pressure drop functions as a maximum allowed pressure drop per tray. No adjustment is done if the pressure drop is below this specified pressure drop.

Packing design automatically finds the diameter resulting in the specified pressure drop (with the selected pressure drop model). This is done by using a linear search technique as the different packing pressure drop correlations can behave quite irregularly. The maximum allowed pressure drop is the flooding pressure drop as specified or computed from Kister's correlation and the packing factor. If the pressure drop is specified to be very low the
column diameter might converge to unrealistic diameters. A zero or larger than flooding pressure drop specification results in a 70 % fraction of flooding design.

5.6.4 Optimizing

This tray design only method tries to optimize the tray design for the following four aspects:

- Cost
- Separation
- Pressure drop
- Flexibility

However, this particular design mode is not yet available.

Symbol List

\(a_d\) Interfacial area density \((m^2/m^3)\)
\(a_I\) Interfacial area \((m^2)\)
\(A_h\) Hole area \((m^2)\)
\(A_{b, A_{bub}}\) Bubbling area \((m^2)\)
\(A_d\) Downcomer area \((m^2)\)
\(c\) Number of components,
\(M\) Molar concentration \((kmol/m^3)\)
\(d_h\) Hole diameter \((m)\)
\(D\) Binary diffusivity coefficient \((m^2/s)\)
\(D_c\) Column diameter \((m)\)
\(D_e\) Eddy dispersion coefficient \((m^2/s)\)
\(e\) Energy transfer rate \((J/s)\)
\(f_{ij}\) Component \(i\) feed flow to stage \(j\) \((kmol/s)\)
\(f_{1, f_{2, f_{3}}}\) Design adjustment factors
\(F_j\) Total feed flow rate to stage \(j\) \((kmol/s)\)
\(F_p\) Packing factor \((1/m)\)
\(F_s\) F factor \(F_s = U_v \sqrt{\rho V} \left(kg^{0.5}/m^{0.5}s\right)\)
\(FF\) Fraction of flooding
\(FP\) Flow parameter \(FP = M_L/M_V \sqrt{\rho_L^V/\rho_L^G}\)
\(Fr\) Froude number
\(g\) Gravitational constant, 9.81 \((m/s^2)\)
Interlinked flow rate (kmol/s)
Heat transfer coefficient (J/m² K s)
Clearance height under downcomer (m)
Clear liquid height (m)
Dry tray pressure drop height (m)
Downcomer backup liquid height (m)
Froth height (m)
Liquid height at tray inlet (m)
Liquid gradient pressure drop height (m)
Liquid pressure drop height (m)
Height of liquid over weir (m)
Residual pressure drop liquid height (m)
Wet tray pressure drop liquid height (m)
Weir height (m)
Liquid height pressure loss under downcomer (m)
Molar enthalpy (J/kmol)
Partial molar enthalpy of component i (J/kmol)
Molar diffusion flux (kmol/m² s)
Binary mass transfer coefficient (m/s)
K-value or equilibrium ratio component i: \( K_i = y_i / x_i \)
Liquid flow rate (kmol/s)
Lewis number (Le = Sc/Pr)
Mass flow rate (kg/s)
Mass transfer rate (kmol/s)
Number of stages
Hole pitch (m),
Pressure (Pa)
Pressure drop (Pa)
Maximum design pressure drop (Pa/tray or Pa/m)
Prandtl number
Heat input (J/s)
Volumetric flow over the weir (m³/s)
Ratio sidestream to internal flow
Matrix defined by (5.13) and (5.14)
Schmidt number
System derating factor
Residence time (s)
Valve thickness (m)
Temperature (K)
Tray spacing (m)
Vapor flow rate (kmol/s)
Weber number
Weir length (m)
Liquid mole fraction
Vapor mole fraction
Mole fraction

Greek:
\( \alpha \) Fraction liquid in froth
\( \beta \) Fractional free area \( \beta = A_h/A_b \)
\( \phi \) Fractional entrainment
\( \rho \) Density \( (kg/m^3) \)
\( \sigma \) Surface tension \( (N/m) \)
\( \eta \) Viscosity \( (Pa\ s) \)
\( \Gamma \) Thermodynamic matrix
\( \lambda \) Heat conductivity \( (W/m/K) \)

Superscripts:
\( I \) Interfacial
\( L \) Liquid
\( P \) Phase \( P \)
\( V \) Vapor

Subscripts:
\( flood \) at flooding conditions
\( i \) component \( i \)
\( j \) stage \( j \),
\( spec \) specified
\( t \) total
\( \nu \) from interlinking stage \( \nu \)

References


R. Billet, *Distillation Engineering?*, Heyden (1979?).


Leva, (1953?).


Chapter 6

Nonequilibrium Extraction

This chapter deals especially with the application of the nonequilibrium model to the modelling of extraction columns. In such operations the two phases present are both liquids instead of a liquid and a vapor as in the case of distillation, stripping, or absorption. This requires fundamentally different mass transfer coefficients and flow models, as well as a completely new design method, that an entire chapter is devoted to the subject.

6.1 Introduction

Nonequilibrium extraction uses the same model as described in the nonequilibrium section, with the exception that there is no vapor. Instead we have a light and a heavy liquid phase, where the light liquid behaves as the vapor with, of course, liquid-like properties. If the heavy phase (L) is lighter than the light phase (V) the program stops. However, either phase (that is, L or V) can be the disperse phase. The user must specify which is the disperse phase, since this changes the design and the calculation of MTC’s. Currently sieve trays, structured and random packed columns, rotating disc contacters, and spray columns are supported as internals (as well as equilibrium stages with a specified stage efficiency). The K-values must be the Liquid-Liquid model, which uses activity coefficients. The energy balance can be ignored (Enthalpy=None) or included. In case it is ignored the column temperature is dictated by that of the feeds, and linear interpolation is used to provide a column temperature profile. A specific temperature profile can be imposed if the energy balance is ignored and user temperature initialization is supplied. Default values for the total interfacial area and mass transfer coefficients are: \( A_i = 100 \, m^2 \), \( k_d = 10^{-5} \) and \( k_c = 10^{-4} \, m/s \). Mass transfer in coalescing layers and jet zones are neglected (they could be modeled by a special stage for packed/RDC columns). Thus, only the drop rise zone is taken into account for mass transfer.
Current limitations of the nonequilibrium extraction model are:

- No efficiencies are back-calculated (yet)
- Limited number of mass transfer coefficient correlation
- No comparisons of simulations with experiment performed

### 6.2 Sieve trays

**ChemSep** will attempt to design the extraction column if no design is specified, this design method is adapted from the notes by R. Krishna.

#### 6.2.1 Design

The default free area ratio is 5\%, tray spacing is 0.4 meter, and the clearance under the downcomer a quarter of the tray spacing. There is no weir. The hole diameter is set by default to:

\[
x = \sqrt{\frac{\sigma}{\Delta \rho g}}
\]

(6.1)

\[
d_h = 1.8x
\]

(6.2)

but \(d_h\) is limited (if supplied) by:

\[0.5x < d_h < \pi x\]

(6.3)

and the practical limits (overriding):

\[3 \text{mm} < d_h < 8 \text{mm}\]

(6.4)

The hole velocity is computed with:

\[
Eo = \frac{\Delta \rho g d_h^3}{\sigma}
\]

(6.5)

\[
We = 4.33 Eo^{-0.26}
\]

(6.6)

\[
U_h = \sqrt{\frac{We \sigma}{\rho d_h}}
\]

(6.7)

If the hole velocity is less than 0.15 (m/s) then its design value is kept at 0.15 (m/s). The Froude number is computed from

\[
Fr = \frac{U_h^2}{gd_h}
\]

(6.8)
For $Eo$ is less than 0.4 the Sauter mean droplet diameter is computed by:

$$d_p = Eo^{-0.4} \left( 2.13 \left( \frac{\Delta \rho}{\rho_d} \right)^{0.67} + \exp(-0.13Fr) \right) d_h$$

otherwise

$$d_p = Eo^{-0.42} \left( 1.24 + \exp(-Fr^{0.42}) \right) d_h$$

(6.9)

(6.10)

The hole area is

$$A_h = \frac{Q_d}{U_h}$$

(6.11)

The ratio of the hole area over the active area (free area ratio, $f$) is limited between 1 and 20%.

$$A_a = A_h/f$$

(6.12)

The hole pitch can be computed if the hole diameter and free area ratio are known. The downcomer velocity can be computed if a minimum droplet diameter, $d_{min}$, is assumed which will not be entrained. The downcomer velocity equals the velocity of the continuous phase, $U_c$:

$$U_c = 0.249d_{min} \left( \frac{g(\Delta \rho)^2}{\rho_c \eta_c} \right)^{0.33}$$

(6.13)

This droplet diameter is taken to be 0.5 mm. With $U_c$ known we can compute the downcomer area:

$$A_d = Q_c/U_c$$

(6.14)

The total area is equal to two downcomer areas plus the active area and 0.5 % area for support etc.:

$$A_t = (A_a + 2A_d)/0.995$$

(6.15)

With the total tray area known the column diameter can be computed. The net area for the disperse phase, $A_n$, and the disperse velocity, $U_d$, are:

$$A_n = A_d + A_d$$

(6.16)

$$U_d = \frac{Q_d}{A_n}$$

(6.17)

Next the dispersed phase velocity holdup and slip velocity are computed. The slip velocity ($V_s$) is guessed at one tenth of the disperse phase velocity, making the disperse phase holdup equal to a tenth since it is defined as

$$\phi_d = \frac{U_d}{V_s}$$

(6.18)

The slip velocity (which is a function of the dispersed phase holdup and needs to be obtained iteratively) can be calculated from:

$$V_s = \sqrt{2.725gd_p \left( \frac{\Delta \rho}{\rho_c} \right) \left( \frac{1 - \phi_d}{1 + \phi_d^{0.33}} \right)^{1.834}}$$

(6.19)
After the dispersed phase holdup is computed (it depends on $V$) it is checked to be within 1 and 20 % for standard operation conditions. If it is too small the free area ratio is increased, if it is too large the free area ratio is decreased (each by 5 %) till it is within the desired range.

The Weber number

$$We = \frac{\rho_d U_h^2 d_p}{\sigma}$$  \hspace{1cm} (6.20)

must be larger than 2 to ensure all holes produce drops (i.e. to avoid inactive holes, see Seibert and Fair, 1988).

The height of the coalesced layer is (according to Treybal, 1980):

$$h_c = \frac{(U_h^2 - U_d^2) \rho_d}{2g C_d^2 \Delta \rho} + \frac{4.5 U_c \rho_c}{2g \Delta \rho} + \frac{6\sigma}{d_p g \Delta \rho}$$  \hspace{1cm} (6.21)

(with $C_d = 0.67$). The first term is height to overcome flow through the orifices, the second for friction losses due to contraction/expansion on entry/exit (0.5 + 1.0) and change of direction (2 times 1.5 velocity heads), and the third term for the interfacial tension effects at the holes. The height needs to be larger than 4 cm (to ensure safe operation). If not, then the hole diameter is decreased by 5 % and we repeat the procedure from the hole velocity calculation (6.5).

This design is for a one pass sieve tray, and flow path length, $L_f$ is computed from geometric relations. The weir length is (segmental downcomer):

$$W_i = A_i / L_f$$  \hspace{1cm} (6.22)

The tray thickness is defaulted to a tenth of an inch. To prevent entrainment of droplets, the flow under the downcomer is only allowed to be 50 % higher than the downcomer velocity. If higher, then the downcomer clearance is enlarged until this requirement is met. The tray spacing is adjusted so that the coalesced layer and coalescence zone divided over the length of the downcomer equals the fraction of flooding (multiplied with the system factor).

### 6.2.2 Report

The reported fraction of flooding equals to the ratio of the height of the coalesced layer over the height of the downcomer (according to Seibert and Fair the flooding calculation is within 20 %). The lower operating limit is the ratio of two over the Weber number (to guarantee proper droplet formation).
6.2.3 Mass Transfer Coefficients

The "Handlos-Baron-Treybal" method is used. The hole velocity $U_h$, $Eo$, $Fr$, net area $A_n$, Sauter mean drop diameter $d_p$, disperse velocity $U_d$, slip velocity $V_s$, disperse phase holdup $\phi_d$, $h_c$, and $h_z$ are computed as above (but with fixed design parameters). The interfacial area per unit of volume is

$$A_i = \frac{6\phi_d}{d_p} \quad (6.23)$$

and the drop rising zone (where mass transfer is assumed to take place):

$$h_{drop} = t_s - h_c \quad (6.24)$$

where $t_s$ is the tray spacing. The volume for mass transfer on a tray is

$$V_i = A_n h_{drop} \quad (6.25)$$

The mass transfer coefficients for transport from the disperse phase are (Handlos and Baron, 1957):

$$k_d = \frac{0.00375V_s}{(1 + \eta_d/\eta_c)} \quad (6.26)$$

and for transport from the continuous phase are (Treybal, 1963):

$$k_{c,ij} = 0.725Re_c^{0.43}(1 - \phi_d)V_sNu_c^{-0.58} \quad (6.27)$$

with

$$Re_c = \frac{d_p V_s \rho_c}{\eta_c} \quad (6.28)$$

$$Nu_c = \frac{\eta_c}{\rho_c D_{ij}} \quad (6.29)$$

Note that $k_d$ is not a function of the diffusion coefficient and, thus, is the same for all components.

6.3 Packed columns

Column design and calculation of mass transfer coefficients is done the same way for structured packed column and random packed columns, following the methods and correlations as outlined by Seibert and Fair (1988).

6.3.1 Design

For mass transfer from the continuous phase to the disperse phase we have $x = 1$ for the calculation of the Sauter mean drop diameter:

$$d_p = 1.15x \sqrt{\frac{\sigma}{\Delta \rho g}} \quad (6.30)$$
The slip velocity of a single droplet at zero disperse phase holdup is given by

$$V_s^o = \sqrt{\frac{4\Delta \rho g d_p}{3\rho_c C_d}}$$

(6.31)

where $Cd = 0.38$ (for high values of Reynolds). Static disperse holdup is:

$$\phi_{ds} = \frac{0.076\,a_p\,d_p}{\xi}$$

(6.32)

where $a_p$ is the packing area and $\xi$ the packing void fraction. The static holdup area and total area are:

$$a_s = 60.076a_p$$

(6.33)

$$a = a_p + a_s$$

(6.34)

The tortuosity is defined as

$$\zeta = \frac{ad_p}{2}$$

(6.35)

The superficial velocity of the continuous phase at the flood point is

$$e = \cos\left(\frac{\pi \zeta}{4}\right)$$

(6.36)

$$U_{cf} = \frac{0.192\xi \times V_s^o}{\left(1.08 + (Q_d/Q_c)/e^2\right)}$$

(6.37)

This needs to be corrected for the fraction of flooding (and system factor):

$$U_c = SF\ FF\ U_{cf}$$

(6.38)

to give the net area

$$A_n = \frac{Q_c}{U_c}$$

(6.39)

from which the packed column diameter ($D_c$) can be calculated.

### 6.3.2 Report

The reported fraction of flooding is the quotient of computed $U_c$ to $U_{cf}$ as discussed above. The dispersion coefficients are given by (Vermeulen et al., 1966):

$$\log \frac{E_d}{Vcd_p} = 0.046\frac{V_c}{V_d} + 0.301$$

(6.40)

$$\log \frac{E_c}{Vcd_p} = 0.161\frac{V_c}{V_d} + 0.347$$

(6.41)

where $d_p$ is the packing diameter.
6.3.3 Mass Transfer Coefficients

The method of Seibert and Fair (1988) is used. The phase velocities are computed by

\[ U_c = \frac{Q_c}{A_n} \]  
\[ U_d = \frac{Q_d}{A_n} \]  

(6.42) \hspace{1cm} (6.43)

The drop diameter \( d_p \), slip velocity \( V_s^o \), area \( a \), static holdup area \( a_s \), and tortuosity \( \zeta \) are calculated as above. Then the disperse phase holdup, \( \phi_d \), is determined iteratively (starting at 0.1) from:

\[ f(\phi_d) = \exp\left(-\frac{6\phi_d}{\pi}\right) \]  
\[ \phi_d = \frac{U_d}{\xi(V_s^o f(\phi_d) - U_c)\zeta^2} \]  

(6.44) \hspace{1cm} (6.45)

Then the slip velocity is

\[ V_s = V_s^o f(\phi_d)c + (1 - c)U_c \]  

(6.46)

since \( U_d = V_s^o f(\phi_d) \). The mass transfer coefficient for the disperse phase is computed by:

\[ \phi = \frac{\sqrt{Sc_d}}{(1 + \eta_d/\eta_c)} \]  
\[ \phi > 6 : k_{d,ij} = \frac{0.023V_s}{\sqrt{Sc_d}} \]  
\[ \phi < 6 : k_d = \frac{0.00375V_s}{(1 + \eta_d/\eta_c)} \]  
\[ Sc_d = \frac{\eta_d}{\rho_d D_{d,ij}} \]  

(6.47) \hspace{1cm} (6.48) \hspace{1cm} (6.49) \hspace{1cm} (6.50) \hspace{1cm} (6.51)

If \( \phi \) is larger than 6 the Laddha and Degaleesan correlation is used otherwise the Handlos-Baron method. For the mass transfer coefficient in the continuous phase:

\[ Sh_c = 0.698Re_c^{0.5}Sc_c^{0.4}(1 - \phi_d) \]  
\[ k_{c,ij} = \frac{Sh_c D_{c,ij}}{d_p} \]  
\[ Re_c = \frac{\rho_c V_s d_p}{\eta_c} \]  
\[ Sc_c = \frac{\eta_c}{\rho_c D_{c,ij}} \]  

(6.52) \hspace{1cm} (6.53) \hspace{1cm} (6.54) \hspace{1cm} (6.55)

The interfacial area per unit volume is:

\[ a_i = \frac{6\xi \phi_d}{d_p} \]  

(6.56)
The total interfacial area in a stage is the stage height times the net area times the interfacial area per unit volume:

\[ a_{i,tot} = a_i A_n h_{stage} \] (6.57)

### 6.4 Rotating Disk Contactors

This design method is based on the *Handbook of Solvent Extraction* (chapter 13.1) and notes by R. Krishna.

#### 6.4.1 Design

The phase ratio \( \alpha \) is

\[ \alpha = \frac{Q_d}{Q_c} \] (6.58)

The maximum stable drop diameter is

\[ u_0 = 0.9 \left( \frac{g \Delta \rho}{\rho_c \rho_d^{1/21}} \right)^{5/21} \sigma^{6/21} \] (6.59)

\[ d_{p,max} = \frac{\sigma}{\rho_c u_0^2} \] (6.60)

A stable drop diameter is selected as half of the maximum diameter

\[ d_p = 0.5d_{p,max} \] (6.61)

and the required power input \( (P_i = N^3 R^5 / HD^2) \) is computed

\[ e = \left( \frac{0.25}{d_p} \right)^{0.6} \left( \frac{\sigma}{\rho_c} \right)^{0.6} \] (6.62)

\[ P_i = \frac{\pi e}{4C_p} \] (6.63)

\( (C_p = 0.03 \text{ for } Re > 10^5) \). If no column diameter is known, an estimate is made from assuming a cross-sectional area for a combined velocity of 0.05 m/s with:

\[ A_c = (Q_c + Q_d)/0.05 \] (6.64)

The required rotational speed (using these standard ratios) is then

\[ N = \left( \frac{P_i}{A_c^2 D_c^2} \right)^{0.33} \] (6.65)
Now the slip-velocity can be calculated using a correlation from Kung and Beckman (1961):

\[
\frac{V_s \eta_c}{\sigma} = \left( \frac{\Delta \rho}{\rho_c} \right)^{0.9} \left( \frac{S}{R} \right)^{2.3} \left( \frac{H}{R} \right)^{0.9} \left( \frac{R}{D} \right)^{2.6} \left( \frac{g}{RN^2} \right)
\]

(6.66)

The disperse holdup at flood is determined from

\[
\phi_d = \frac{\sqrt{\alpha^2 + 8\alpha - 3\alpha}}{4(1 - \alpha)}
\]

(6.67)

from which the continuous phase velocity at flood can be determined with

\[
U_{c,f} = V_s(1 - \phi_d)^2(1 - 2\phi_d)
\]

(6.68)

Correction for fraction of flooding (and system factor) gives

\[
U_c = SF \frac{FF}{U_{c,f}}
\]

(6.69)

from which the column area and diamater can be calculated

\[
A_c = \frac{Q_c}{U_c}
\]

(6.70)

The rotor diameter \(R\), stator diameter \(S\), and the height of the compartment have standard ratios with respect to the column diameter \(D_c\)

\[
R = 0.6D_c
\]

(6.71)

\[
S = 0.7D_c
\]

(6.72)

\[
H = 0.1D_c
\]

(6.73)

so the size of the column is determined. Below a Renolds number of \(10^5\) \(C_p\) becomes a function of the Renolds number. Normally RDC's are operated in the regime above \(10^5\) so the Renolds number is computed by

\[
Re_d = \frac{\rho_d NR^2}{\eta_d}
\]

(6.74)

and a smaller diameter is selected (and the calculations repeated) if necessary. On re-design the layout of the stage with the largest diameter is used for the entire section.

6.4.2 Report

The reported fraction of flooding is the quotient of computed \(U_c\) over \(U_{c,f}\) as discussed above. The operating velocity is proportional to the slip velocity and so inverse proportional to the square of the rotation speed. One of the design rules was to keep the disperse Reynolds number larger than \(10^5\) so the lower operating limit is defined as:

\[
\left( \frac{10^5}{Re_d} \right)^2
\]

(6.75)
Stemerding et al. (1963) gave a correlation for the axial dispersion coefficient for the continuous phase
\[
\frac{E_c}{V_e H} = 0.5 + 0.012 N R (S/D)^2 / V_c
\]  
(6.76)

The disperse dispersion coefficient is set to twice this number.

### 6.4.3 Mass Transfer Coefficients

The method of "Kronig-Brink-Rowe" is used. Phase ratio \( \alpha \), energy input \( P_i \) (from \( N, R, H, \) and \( D_c \)) are computed as above. The drop diameter is computed from
\[
C_p = 0.03
\]  
(6.77)
\[
e = \frac{4 C_p P_i}{\pi}
\]  
(6.78)
\[
d_p = \frac{0.25 (\sigma / e)^{0.6}}{\rho_c^{0.4}}
\]  
(6.79)

The dispersed holdup \( \phi_d \) is calculated iteratively as above and the slip velocity is determined as described above (with 6.66). The mass transfer coefficients are:
\[
Sh_d = 10.0
\]  
(6.80)
\[
k_{d,ij} = \frac{Sh_d D_{d,ij}}{d_p}
\]  
(6.81)
\[
Sh_c = 2 + 0.42 R e_c^{0.62} S c_c^{0.36}
\]  
(6.82)
\[
k_{c,ij} = \frac{Sh_c D_{c,ij}}{d_p}
\]  
(6.83)

with
\[
R e_c = \frac{\rho_d d_p^{1.33} e^{0.33}}{\eta_c}
\]  
(6.84)
\[
S c_c = \frac{\eta_c}{\rho_c D_{c,ij}}
\]  
(6.85)

The interfacial area per unit volume is
\[
a_i = \frac{6 \phi_d}{d_p}
\]  
(6.86)

Alternatively the "Rose-Kintner-Garner-Tayeban" method can be used:
\[
Sh_c = 0.6 \sqrt{R e_c \sqrt{S c_c}}
\]  
(6.87)
\[
b = \frac{d_p^{0.225}}{1.242}
\]  
(6.88)
\[
\omega = \frac{8 \sigma b n (n + 1) (n - 1) (n + 2)}{d_p (n + 1) \rho_d + n \rho_c}
\]  
(6.89)
\[
k_d = 0.45 \sqrt{D_{d,ij} \omega}
\]  
(6.90)

where \( n = 2 \), and \( d_p \) is in cm for the calculation of \( b \) and \( \omega \).
6.5 Spray columns

This design method is adapted from Jordan (1968) and Lo et al. (1983).

6.5.1 Design

The height of a stage in a spray column is set to the default value of 0.4 m and the hole diameter in the distributor to 0.005 m. The hole velocity \( U_o \) in the distributor is set to 0.1 m/s from which the total hole area is then:

\[
A_o = Q_d / U_o \tag{6.91}
\]

The droplet diameter can be calculated from (Vedaiyan et al., 1972):

\[
d_p = 1.592 \left( \frac{U_o^2}{2g\sigma} \right)^{-0.067} \sqrt{\frac{\sigma}{g\Delta\rho}} \tag{6.92}
\]

The flood velocity of the continuous phase is (Treybal, 1963):

\[
U_{cf} = \frac{0.3894\Delta\rho^{0.28}}{ \left[ 0.2165\rho_c^{0.075} \sqrt{\rho_c + 0.2670\rho_p^{0.056}} \sqrt{\rho_d^2} \right]^{1/2}} \tag{6.93}
\]

where \( \alpha = Q_d / Q_c \). The disperse holdup at flood is

\[
\phi_{df} = \frac{\sqrt{\alpha^2 + 8\alpha - 3\alpha}}{4(1 - \alpha)} \tag{6.94}
\]

The velocity of the continuous phase is then

\[
U_c = FF \cdot SF \cdot U_{cf} \tag{6.95}
\]

and the column area

\[
A_c = Q_c / U_c \tag{6.96}
\]

from which the column diameter can be calculated (The column area must also be larger than the total hole area, if not, the column area is set to four times the hole area).

6.5.2 Report

The fraction of flooding reported is calculated as

\[
FF = \frac{U_c}{SF \cdot U_{cf}} \tag{6.97}
\]
where $U_{cf}$ is computed as in the spray column design and $U_c = A_c/Q_c$. No lower operating limit is calculated. The dispersion coefficient for the continuous phase is (Vermulnen et al., 1966):

$$\frac{E_c}{V_cH} = 7.2\sqrt{U_dD_c}$$  \hspace{1cm} (6.98)

Since the dispersion coefficient for the disperse phase is unknown it is set equal to that for the continuous phase.

### 6.5.3 Mass Transfer Coefficients

The transition drop size below which droplets become stagnant is calculated from

$$P = \frac{\rho_c^2 \sigma^4}{g \eta_c^2 \Delta \rho}$$  \hspace{1cm} (6.99)

$$d_{p,t} = 7.25 \sqrt{\frac{\sigma}{g \Delta \rho P^{0.15}}}$$  \hspace{1cm} (6.100)

The drop terminal velocity is (Satish et al., 1974):

$$V_t = 1.088 \left( \frac{U_o^2}{2g d_o} \right)^{-0.082} \left( \frac{\sigma g \Delta \rho}{\rho_c^2} \right)^{1/4}$$  \hspace{1cm} (6.101)

With the continuous operating and flood velocities the fraction of flooding is calculated and then the disperse phase holdup is

$$\phi_d = FF \phi_{df}$$  \hspace{1cm} (6.102)

and the slip velocity

$$V_s = (1 - \phi_d) V_t$$  \hspace{1cm} (6.103)

If the drops are stagnant ($d_p < d_{p,t}$) the disperse MTC is computed from

$$k_{d,ij} = 18.9 D_{d,ij} / d_p$$  \hspace{1cm} (6.104)

else the Handlos-Baron correlation (1957) is used:

$$k_d = \frac{0.00375 V_s}{(1 + \eta_d / \eta_c)}$$  \hspace{1cm} (6.105)

For the continuous phase MTC we use (Ruby and Elgin, 1955)

$$k_c = 0.725 R_{ec}^{-0.43} S_{ec}^{-0.58} (1 - \phi_d) V_s$$  \hspace{1cm} (6.106)

where

$$R_{ec} = \frac{d_p V_s \rho_c / \eta_c}{\eta_c / \rho_c D_{c,ij}}$$  \hspace{1cm} (6.107)

$$S_{ec} = \frac{\eta_c}{\rho_c D_{c,ij}}$$  \hspace{1cm} (6.108)

The interfacial area for mass transfer per unit of volume is

$$A_i = \frac{6 \phi_d}{d_p}$$  \hspace{1cm} (6.109)
6.6 Modeling Backflow

The backflows in the column are computed from the dispersion coefficients with:

\[
\alpha_d = \frac{E_d}{V_dH} - 0.5 \quad (6.110)
\]

\[
\alpha_c = \frac{E_c}{V_cH} - 0.5 \quad (6.111)
\]

where \(\alpha\) is the fractional backflow ("entrainment") in the stage, and \(H\) is the stage height.

For spray columns (Perry, 1984):

\[
E_c = 7.2\sqrt{V_cD_c} \quad (6.112)
\]

For packed columns:

\[
\log \frac{E_d}{V_d^{1F}} = 0.046 \frac{V_c}{V_d} + 0.301 \quad (6.113)
\]

\[
\log \frac{E_c}{V_c^{1F}} = 0.161 \frac{V_c}{V_d} + 0.347 \quad (6.114)
\]

For a RDC:

\[
E_c = 0.5HV_c + 0.012RNH \left( \frac{S}{D_c} \right) \quad (6.115)
\]

\[
E_d = FE_c \quad (6.116)
\]

where \(F\) is calculated by

\[
F = 4.210^5 \left( \frac{V_d}{h} \right)^{3.3} \quad (6.117)
\]

and must be larger or equal than one. Krishna uses:

\[
E_c = \frac{0.5HU_c}{(1 - \Phi_d)} + 0.012RNH \left( \frac{S}{D_c} \right) \quad (6.118)
\]

\[
E_d = \frac{0.5HU_d}{\Phi_d} + 0.024RNH \left( \frac{S}{D_c} \right) \quad (6.119)
\]

Symbol List

- \(a_p\)  Packing area per unit volume \((m^2/m^3)\)
- \(a_s\)  Static holdup area per unit volume \((m^2/m^3)\)
- \(A_a\)  Total tray active area \((m^2)\)
- \(A_d\)  Downcomer area \((m^2)\)
- \(A_i\)  Interfacial area per unit volume \((m^2/m^3)\)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_h$</td>
<td>Total tray hole area ($m^2$)</td>
</tr>
<tr>
<td>$A_n$</td>
<td>Netto tray area ($m^2$), $A_n = A_a + A_d$</td>
</tr>
<tr>
<td>$A_t$</td>
<td>Total tray area ($m^2$)</td>
</tr>
<tr>
<td>$C_d$</td>
<td>Drag coefficient</td>
</tr>
<tr>
<td>$D$</td>
<td>Binary diffusion coefficient ($m^2/s$)</td>
</tr>
<tr>
<td>$D_c$</td>
<td>Column diameter ($m$)</td>
</tr>
<tr>
<td>$d_e$</td>
<td>Effective drop diameter ($m$)</td>
</tr>
<tr>
<td>$d_h$</td>
<td>Hole diameter ($m$)</td>
</tr>
<tr>
<td>$d_{min}$</td>
<td>Minimum droplet diameter ($m$)</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Sauter mean drop diameter ($m$)</td>
</tr>
<tr>
<td>$E_o$</td>
<td>Eotvos number ($\Delta \rho g d_h / \sigma$)</td>
</tr>
<tr>
<td>$f$</td>
<td>Free area ratio ($A_h / A_a$)</td>
</tr>
<tr>
<td>$F$</td>
<td>Molar flow ($kmol/s$)</td>
</tr>
<tr>
<td>$Fr$</td>
<td>Froude number ($U_h^2 / gd_h$)</td>
</tr>
<tr>
<td>$FF$</td>
<td>Fraction of flooding</td>
</tr>
<tr>
<td>$g, g_c$</td>
<td>Gravitational constant, 9.81 ($m/s^2$)</td>
</tr>
<tr>
<td>$H$</td>
<td>RDC compartment height ($m$)</td>
</tr>
<tr>
<td>$h_c$</td>
<td>Height of coalesced layer ($m$)</td>
</tr>
<tr>
<td>$h, h_{drop}$</td>
<td>Height of drop rising zone ($m$)</td>
</tr>
<tr>
<td>$h_{stage}$</td>
<td>Stage height for packed column ($m$)</td>
</tr>
<tr>
<td>$k$</td>
<td>Binary mass transfer coefficient ($m/s$)</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Molecular weight ($kg/kmol$)</td>
</tr>
<tr>
<td>$N$</td>
<td>Rotation speed ($rad/s$)</td>
</tr>
<tr>
<td>$Nu$</td>
<td>Nusselt number</td>
</tr>
<tr>
<td>$Pe$</td>
<td>Peclet number</td>
</tr>
<tr>
<td>$P_i$</td>
<td>Power input (?)</td>
</tr>
<tr>
<td>$Q$</td>
<td>Volumetric flow ($m^3/s$)</td>
</tr>
<tr>
<td>$R$</td>
<td>Rotor diameter ($m$)</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$S$</td>
<td>Inner stator diameter ($m$)</td>
</tr>
<tr>
<td>$Sc$</td>
<td>Schmidt number</td>
</tr>
<tr>
<td>$Sh$</td>
<td>Sherwood number</td>
</tr>
<tr>
<td>$SF$</td>
<td>System derating factor</td>
</tr>
<tr>
<td>$t$</td>
<td>Contact time ($s$)</td>
</tr>
<tr>
<td>$t_s$</td>
<td>Tray spacing ($m$)</td>
</tr>
<tr>
<td>$U_{c,U_d}$</td>
<td>Continuous, disperse velocity ($m/s$)</td>
</tr>
<tr>
<td>$U_{c,f}$</td>
<td>Continuous phase superficial velocity at flood ($m/s$)</td>
</tr>
<tr>
<td>$U_h$</td>
<td>Hole diameter ($m/s$)</td>
</tr>
<tr>
<td>$V_i$</td>
<td>Tray volume for interfacial mass transport ($m^3$)</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Slip velocity ($m/s$)</td>
</tr>
<tr>
<td>$V_s^0$</td>
<td>Slip velocity at zero disperse phase holdup ($m/s$)</td>
</tr>
<tr>
<td>$We$</td>
<td>Weber number ($\rho d U_h^2 d_p / \sigma$)</td>
</tr>
<tr>
<td>$W_t$</td>
<td>Weir length ($m$)</td>
</tr>
</tbody>
</table>
Greek:
\[ \alpha \] Phase ratio \((Q_d/Q_c)\)
\[ \rho \] Mass density \((kg/m^3)\)
\[ \phi_d \] Disperse phase holdup fraction
\[ \phi_{ds} \] Static disperse phase holdup fraction
\[ \sigma \] Interfacial tension \((N/m)\)
\[ \eta \] Liquid viscosity \((Pa.s)\)
\[ \mu \] Kinematic viscosity \((\eta/\rho)\)
\[ \zeta \] Tortuosity
\[ \kappa \]
\[ \delta \]

Subscripts:
\[ c \] Continuous phase
\[ d \] Disperse phase,
\[ \text{Downcomer} \]
\[ i \] Interface,
\[ \text{Component i} \]
\[ j \] Component j

References


R. Krishna, S.M. Nanoti, A.N. Goswami, "Mass-Transfer Efficiency of Sieve Tray Extraction


Mass Transfer Coefficient correlations

Mass Transfer Coefficients correlations for the continuous phase (chapter 3.4, Handbook of Solvent Extraction):

- Rowe et al. (1965):
  \[ S h_c = A + B Re_d^{0.5} Sc_c^{0.33} \]  
  with \( A = 2 \) and \( B = 0.79 \).

- Griffith (1960); \( A = 2 \) and \( B = 1.13 \).

- Weber (1975):
  \[ S h_c = \frac{2}{\pi} \sqrt{1 - Re_d^{-0.5} \left( 2.89 + 2.15 \mu_t^{0.64} \right)^2} \sqrt{Pe} \]  
  where \( Pe = Re_d Sc_c \)  
  \[ (6.121) \]

- Garner et al. (1959):
  \[ S h_c = -126 + 1.8 Re_d^{0.5} Sc_c^{0.42} \]  
  \[ (6.123) \]

- Thorsen and Terjesen (1959): for pure solvents:
  \[ S h_c = -178 + 3.62 Re_d^{0.5} Sc_c^{0.33} \]  
  \[ (6.124) \]
Mass Transfer Coefficients correlations for the disperse phase (chapter 3.4, Handbook of Solvent Extraction):

- Kronig and Brink (1950):
  \[ Sh_d = \frac{k_d \phi_d d_p}{D_d} = 16.7 \] (6.125)
  for \( Re_d < 50 \).

- Handlos and Baron (1957):
  \[ k_d = \frac{0.00375V_s}{1 + \frac{\mu_d}{\mu_c}} \] (6.126)

- Skelland and Wellek (1964):
  \[ Sh_d = 0.32Re^{0.68} \left( \frac{\sigma^3 \rho_c^2}{\eta \mu_c^3 \Delta \rho} \right)^{0.30} \left( \frac{4D_{dij} t_c}{d_d^2} \right)^{-0.14} \] (6.127)

- Rozen and Bezzubova (1968):
  \[ a : Sh_d = 0.32Re^{0.63}Sc^{0.50} \left( 1 + \frac{\mu_d}{\mu_c} \right)^{-0.5} \] (6.128)
  \[ b : Sh_d = 7.5 \times 10^{-5}Re^{2.9}Sc^{0.6} \left( 1 + \frac{\mu_d}{\mu_c} \right)^{-0.5} \] (6.129)
  for medium (a) and large (b) droplets.

where Reynolds, Schmidt, and Sherwood numbers are defined as:

\[ Re = \frac{d_p \rho V_s}{\eta} \] (6.130)

\[ Sc = \frac{\eta}{\rho D_{dij}} \] (6.131)

\[ Sh_{ij} = \frac{k_{ij} d_p}{D_{dij}} \] (6.132)

\[ \mu = \frac{\eta}{\rho} \] (6.133)

Table 1 of chapter 10 in the Handbook of Solvent Extraction supplies us with three more models for the drop rise zone. One for stagnant drops (Skelland and Conger, 1973):

\[ k_d = -\left( \frac{d_e}{6t} \right) \left( \frac{\rho_d}{M_d} \right)_{av} \ln \left( 1 - \pi D_{vd}^{0.5} \frac{t}{0.5d_e} \right) \] (6.134)

\[ k_c = 0.74 \left( \frac{D_{wc}}{d_e} \right) \left( \frac{\rho c}{M_c} \right)_{av} \left( \frac{d_e V_s \rho c}{\mu_c} \right)^{0.5} \left( \frac{\mu c}{\rho c D_{wc}} \right)^{0.333} \] (6.135)
for circulating drops (Treybal, 1963):

\[
k_d = 31.4 \left( \frac{D_{vd}}{d_c} \right) \left( \frac{\rho_d}{M_d} \right)_{av} \left( \frac{4D_{vd} \tau}{d_c^2} \right)^{0.34} \left( \frac{\mu_d}{\rho_d D_{vd}} \right)^{-0.125} \left( \frac{d_e V_s^2 \rho_c}{\sigma} \right)^{0.37} \quad (6.136)
\]

\[
k_c = 0.725 \left( \frac{\rho_c}{M_c} \right)_{av} \left( \frac{d_e V_s \rho_c}{\mu_c} \right)^{-0.34} \left( \frac{\mu_c}{\rho_c D_{vc}} \right)^{-0.58} V_t(1 - \phi_d) \quad (6.137)
\]

and for oscillating drops (Skelland and Conger, 1973):

\[
k_d = 0.32 \left( \frac{D_{vd}}{d_c} \right) \left( \frac{\rho_d}{M_d} \right)_{av} \left( \frac{4D_{vd} \dot{d}^t}{d_c^2} \right)^{-0.14} \left( \frac{d_e V_s \rho_c}{\mu_c} \right)^{0.68} \left( \frac{\sigma^3 \rho_c^2}{\mu^4 g \Delta \rho} \right)^{0.10} \quad (6.138)
\]

\[
k_c = \left( \frac{D_{vc}}{d_c} \right) \left( \frac{\rho_c}{M_c} \right)_{av} \left( \frac{d_e V_s \rho_c}{\mu_c} \right)^{-0.34} \left[ 50 + 0.0085 \left( \frac{d_e V_s \rho_c}{\mu_c} \right)^{1.0} \left( \frac{\mu_c}{\rho_c D_{vc}} \right)^{0.7} \right] \quad (6.139)
\]

where \( t = h/V_t \) (with \( h \) as the height of the drop rise zone) and \( V_t = V_t(1 - \phi_d) \). Perry’s also supplies us with some more correlations. There we find that (6.137) is from Ruby and Elgin (1955) and is to be applied for circulating drops. Another correlation for the continuous mass transfer coefficients for circulating drops is by Hughmark (1967):

\[
\frac{k_c d_p}{D_c} = \left[ 2 + 0.463 Re^{0.4845} Sc^{0.339} \left( \frac{d_p g^{1/3}}{D_c^{1/3}} \right)^{0.072} \right] F \quad (6.140)
\]

\[
F = 0.281 + 1.615 \kappa + 3.73 \kappa^2 - 1.874 \kappa^3 \quad (6.141)
\]

\[
\kappa = Re^{1/8} \left( \frac{\mu_c}{\mu_d} \right)^{1/4} \left( \frac{\mu_c V_s}{\sigma g c} \right)^{1/6} \quad (6.142)
\]

where \( Re \) is the droplet Reynolds number. A correlation for the disperse mass transfer coefficient for oscillating droplets by Rose and Kinter (1966) is:

\[
k_d = \sqrt{\frac{4D_d \omega}{\pi}} \left( 1 + \delta + \frac{3}{8} \delta^2 \right) \quad (6.143)
\]

\[
\omega = \frac{1}{2\pi} \sqrt{\frac{192 \sigma g_k b}{d_p^2 (3 \rho_d + 2 \rho_c)}} \quad (6.144)
\]

\[
b = 1.052 d_p^{0.225} \quad (6.145)
\]

where \( \delta \) can be taken as 0.2 if unknown.

**RDC’s: Korchinsky**

Korchinsky (1992) summarizes correlations for RDC’s from literature and advises on to use the Kumar and Hartland correlations (1986). They use the following dimensionless groups:

\[
N_1 = \left( \frac{ND_T^2 \rho_c}{\mu_c} \right) \quad (6.146)
\]
The Sauter droplet size is computed by the high Reynolds formula from Kumar and Hartland (1986):

\[
\frac{d_{32}}{D_r} = k N_1^{0.55} \exp(-0.23 N_2) N_3^{-1.3} N_4^{0.75} N_5^{-0.3} N_6^{0.28}
\]  

(6.165)
with $10^3k = 7.01$ for no mass transfer. The Kumar and Hartland disperse holdup:

$$\phi_d = [k_1 + k_2 N_2] N_7 N_8 N_9 N_10 \left(1 + \frac{V_c}{V_d}\right)^{0.35}$$

(6.166)

where (using all data) $k_1 = 65.73$, $k_2 = 74.20$, $n_1 = 1.24$, $n_2 = -0.34$, $n_3 = -0.049$, and $n_4 = 0.53$. The slip velocity is computed by

$$V_s = [k_6 + k_7 \exp(-1.28N_2)] N_8 N_9 N_10 N_2 N_3 N_4 N_5 N_6 N_7 N_8 N_9 N_10$$

(6.167)

with (for all data) $10^3 k_6 = -5.11$ and $k_7 = 0.20$. The continuous phase dispersion coefficient is given by

$$\frac{E_c}{V_cH} = 0.42 + 0.29 \frac{V_d}{V_c} + \left(0.0126 N_1 + \frac{13.38}{3.18 + N_1}\right) N_1^{-1.08} N_2^{-1.06} N_3^{-0.14} N_4^{-0.28}$$

(6.168)

and the disperse phase coefficients

$$\frac{E_d}{V_dH} = 0.3 \left(\frac{V_c + V_d}{V_d}\right) + 9.37 N_5 N_6^{-0.64} N_7^{-0.7} \phi_d^{-0.9}$$

(6.169)

**Packed columns: Kumar and Hartland**

Kumar and Hartland (1994) developed new correlations for the drop diameter, dispersed phase holdup, slip velocity, and flooding velocities for packed extraction columns using a large database. The Sauter mean droplet size is

$$d_p = C_1 \left[ \frac{\mu_w g^{1/4} \rho_w}{\Delta \rho^{1/4} \sigma^{3/4} \rho_d} \right]^{0.19} \sqrt{\frac{\sigma}{g \Delta \rho \rho_d}}$$

(6.170)

where $C_1$ is 2.54, 2.24, or 3.13 for no mass transfer, transfer from c to d, and from d to c. The dispersed phase holdup is

$$\phi_d = C_2 e^{-1.11} \left(\frac{\Delta \rho}{\rho_c}\right)^{-0.50} \left[ \frac{1}{\alpha_p} \left(\frac{\rho_c g}{\mu_c^2}\right)^{1/3} \right]^{-0.72} \left(\frac{\mu_d}{\mu_c}\right)^{0.10} \left(\frac{V_d}{\rho_c \mu_c}\right)^{1/3} \exp \left[0.95 V_c \left(\frac{\rho_c}{g \mu_c}\right)^{1/3}\right]$$

(6.171)

where $C_2$ is 5.34, 6.16, or 3.76. The slip velocity is

$$V_{slip} = C_3 e^{-0.11} \left(\frac{\Delta \rho}{\rho_c}\right)^{0.40} \left[ \frac{1}{\alpha_p} \left(\frac{\rho_c g}{\mu_c^2}\right)^{1/3} \right]^{0.61} \left(\frac{\mu_d}{\mu_c}\right)^{-0.30} \left(\frac{\rho_c}{g \mu_c}\right)^{-1/3}$$

(6.172)

where $C_3$ is 0.24, 0.21, or 0.31. Or, as function of the dispersed phase holdup:

$$V_{slip} = C_4 e^{-0.17} \left(\frac{\Delta \rho}{\rho_c}\right)^{0.41} \left[ \frac{1}{\alpha_p} \left(\frac{\rho_c g}{\mu_c^2}\right)^{1/3} \right]^{0.59} \left(\frac{\mu_d}{\mu_c}\right)^{-0.30} \left(\frac{\rho_c}{g \mu_c}\right)^{-1/3} (1 - \phi_d)$$

(6.173)
where $C_d$ is 0.30, 0.27, or 0.38. The flooding velocity is:

$$V_{c,f}(1 + \sqrt{R})^2 \sqrt{a_p/g} = \alpha C_1 e^{1.54} \left( \frac{\Delta \rho}{\rho_d} \right)^{0.41} \left[ \frac{1}{a_p} \left( \frac{\rho_c g}{\mu_c^2} \right)^{1/3} \right]^{0.30} \left( \frac{\mu_c}{\sqrt{\Delta \rho \sigma/a_p}} \right)^{0.15}$$

(6.174)

or

$$V_{d,f} \sqrt{\frac{a_p}{g}} = \alpha C_1 e^{1.54} \left( \frac{\Delta \rho}{\rho_d} \right)^{0.41} \left[ \frac{1}{a_p} \left( \frac{\rho_c g}{\mu_c^2} \right)^{1/3} \right]^{0.30} \left( \frac{\mu_c}{\sqrt{\Delta \rho \sigma/a_p}} \right)^{0.15}$$

(6.175)

where $\alpha$ is 1.0 for continuous phase packing wetting and 1.29 for dispersed phase packing wetting.
Chapter 7

Interface and Technical Issues

In this chapter we will briefly discuss ChemSep's internals. We discuss which programs make up ChemSep and explain how they cooperate. All the supporting libraries and files are identified and explained. More information on printing from within ChemSep and other technical issues can be found in this chapter.

7.1 ChemSep Commandline Parameters

The following commandline parameters are optional when you start ChemSep by typing cs at the commandline:

-sXX : where XX = 25, 28, 33, 35, 40, 43, or 50. This will set the number of lines on the screen to the specified number. Especially the 33 and 40 line modes are very handy. The number of lines can also be set in the interface options.

-oFILE.CNF : loads options from FILE.CNF instead of CHEMSEP.CNF.

-kXXXX : stuffs all characters after the -k onto the keyboard buffer as if they were typed in. See the help for macro definitions for the handling of special keys.

-vx : disable the use of extended memory (XMS) for overlays.

-ve : disable the use of expanded memory (EMS) for overlays.

-vbXXXX : to set the buffer size for overlay swapping to the hard disk where XXXX specifies the size in bytes.

Any other parameter will be handled as a Sep-file, which ChemSep will try to load after the introduction screen (the default "sep" extension does not need to be added). The interface
of ChemSep is too large to fit in conventional memory. Therefore, it uses an "overlay" technique to switch parts in and out of conventional memory from XMS, EMS, or the hard disk (in this order). Use the /v options to manipulate what type of memory is used for the overlays. You can not disable the hard disk, as there would be possibly no place for the overlay manager to store unused parts. Normally you should not need to use these options.
To see which type of overlay is used type Ctrl-Y in the interface (which shows also the DOS version, coprocessor type, and memory status).

7.2 ChemSep Environment Variables

In order to solve column problems ChemSep requires more than the standard DOS memory of 640 kilobytes. Either EMS (expanded) or XMS (extended) memory can be used.

7.2.1 CauseWay DOS extender

CauseWay (Devore software) is currently our default DOS extender. Executables linked with this extender start with the "CW" characters. This DOS extender supports memory up to 4 GB (although you won't need that much to run ChemSep!). If physical memory is limited it will use the disk as virtual memory. All options can be set with one environment variable. The format is

```
SET CAUSEWAY=[setting_1;] [setting_2;] [setting_n;]
```

Seven options are available:

- DPMI; force use of DPMI rather than VCPI
- EXTALL; force to use all extended memory, allocate from bottom-up instead of top-down. No other extender memory will be available for other programs
- HIMEM:nnn; set maximum physical memory in kilobytes. If more memory is required by the program it will be allocated from virtual memory
- LOWMEM:nnn; reserve nnn kilobytes of DOS conventional memory for use by other programs (besides default of 32k)
- MAXMEM:nn; set maximum linear address space in Megabytes. This setting is similar to HIMEM but includes the virtual memory
- NOVM; disable all virtual memory use
- SWAP: path; set swap file path. This path takes precedence for choosing the location of a swap file over the regular TEMP and TMP environment variables that are normally used for these files. Useful to specify a path on a local rather than a network drive.

7.2.2 Rational

The DOS Rational extender was our previous choice of DOS extender. Executables linked with this extender start with the "4G" characters. The DOS extender selects EMS and then XMS. You can force the DOS extender to use XMS above EMS by specifying it to use a block of memory larger than the available EMS. For example, the environment variable dos16m=:4m requests a block of memory of 4 MB (use the DOS set command to specify environment variables). If there is more than 4 MB of EMS available the DOS extender will use EMS, otherwise it will try to use 4 MB of XMS. If the physical memory in your machine does not allow you to run a large problem you can use virtual memory which is swapped to your hard disk by using the following environment variable setting: dos4gvm=deleteswap which allows up to 16 MB of virtual memory and deletes the swap file after the run is completed. The virtual memory is swapped to the DOS4GVM.SWP file which is placed in the root directory of the current drive.

7.2.3 SVGA drivers

In case the automatic selection of the Super VGA drivers XVGA16 and XVGA256 select a wrong video chipset, you can set the CHIPSET environment variable to change the detection test. For example SET CHIPSET=VESA,CRRS will set the CHIPSET environment variable so that the Super VGA driver will first test for VESA, if this fails for Cirrus, and if this also fails it will use a generic VGA mode. The chipset codes are (in the standard detection order): EVRX (Everex), CMPQ (Compaq), V7 (Video 7), C&T (Chips & Tech), CRRS (Cirrus), ATI, TSNG (Tseng), OAK, (Oak Technologies), GNOA (Genoa), TRID (Trident), PRDS (Paradise), NCR, AHED (Ahead Systems), S2, VESA.

7.2.4 Printer drivers

The printer drivers also can make use of extended/expanded memory for generating temporary raster files for the printouts. At the moment, no options can be set through environment variables for the memory use of these drivers.
7.3 ChemSep’s Programs

ChemSep is not one program but is split into several executables and associated data files. Before we can explain in detail how ChemSep uses the programs let’s first see what program names are present in the executables directory and what they do:

- CS.EXE: the driver for ChemSep
- CS2.EXE: ChemSep interface
- CSW.EXE: the solve driver
- (CW-)COL2.EXE: COLumnn simulator
- (CW-)NEQ2.EXE: NonEquilibrium column simulator
- CP.EXE: the driver for ChemProp
- CP1.EXE: ChemProp interface
- CL.EXE: ChemLib interface

The drivers acts as the glue between all the interfaces and simulators. It also gives us flexibility in the way we run our programs and hides details from the average user. ChemSep and ChemProp are normally started by running their drivers: CS.EXE and CP.EXE, respectively. However, both ChemProp and ChemLib can be run from within the ChemSep interface through menu options under the input menu.

The "CW-" in front of the calculation programs denotes the DOS extender type that is linked to the executables. CauseWay executables include the DOS extender, the Rational DOS-Extender uses a separate file (DOS4GW.EXE). The executables often need at least two MegaByte of Extended memory in order to run. They also require a 386-based system (minimum) to run. The different DOS extender executables can be selected under Options/DOS-Extender. Check this setting when you get error messages stating that executables with the ”CW-” or ”4G-” are not found. CauseWay is currently our default.

As we support the simulators on other platforms as well, they must also run without the ChemSep interface. That is why we store all information (in- and output) in the problem files, with the .SEP extension. As the simulator must know what problem file to run it checks for the existence of the CHEMSEP.FIL file. If it exists, it will read this name from this file. If the file doesn’t exist or no CHEMSEP.FIL file was found in the current directory, the simulator will prompt you for a SEP file. DOS and Windows executables of the simulators also allow specification of the SEP file on the commandline, making the CHEMSEP.FIL unnecessary.
To build in maximum flexibility we use the CS and CSW drivers. Both these drivers can run the simulators upon cooperation with the CS2.EXE interface. The default configuration makes the interface run the CSW driver which in turn runs the necessary simulator. The CSW driver insures that all the output of the simulator gets written into a window, giving the illusion that the simulator is an integral part of the interface. While solving the problem the interface is swapped out of DOS memory, and swapped back in upon termination of the simulator. In this case the CS driver is not doing anything and the interface can be invoked directly as well.

Alternatively, the interface can write a CHEMSEP.FIL file, exit, and the CS driver reads it. It determines which simulator is requested to run and start it. The simulator will read the CHEMSEP.FIL again and read the name of the SEP file to solve. Upon termination the CS driver restarts the ChemSep interface, telling it which SEP file it was solving. The interface reads the SEP file and deletes the CHEMSEP.FIL file. Again, the CS driver also ensures the output to be written into a window on the screen. If the interface is loaded directly, without the driver, this is not possible. However, the interface will still run the simulator by swapping itself out of memory, and back into memory after the simulator returns control. It will call the simulator directly without writing a CHEMSEP.FIL file. Without any driver the interface can't redirect the output to a window and thus the screen is cleared before and restored after the simulator runs.

Switching between these modes of solving SEP files is done by specifying the user program under the solve options. The default setting is to call the CSW driver (the interface will locate it, don't specify its path!). If the user program is left empty, the interface will write a CHEMSEP.FIL and quit if the CS driver was loaded, else it will call the simulator directly. Only in this case the screen will be cleared (it also requires the least amount of DOS memory). If the interface is swapped out of memory, it is written to extended memory or disk. If, for whatever reason, the swapfile on disk is deleted the interface will not be able to recover and abort to DOS.

If you are running the simulator programs by your self (that is not abnormal) you might like the small utility MAKEFIL to generate your CHEMSEP.FIL file. Since the simulator programs do not delete the CHEMSEP.FIL file you have only to create it once for each new problem. The MAKEFIL program takes as first commandline argument the SEP-file and as (optional) second argument the scrap file name:

```
MAKEFIL <SEP-file> [Temporary file]
```

The CHEMSEP.FIL file will be written in the current directory. If you run under DOS or Windows, you can also specify the SEP-file pathname as commandline parameter to the simulator, and avoid the use of the CHEMSEP.FIL file all together.
As noted in the previous section, *ChemSep* has separate programs for the calculations and interfacing with the user. In order for the Driver to know what is going on, the interface saves information in the CHEMSEP.FIL such as the name of the SEP-file, the program to run, the temporary scrap file name, the user program, the run window coordinates and color as well as the starttime.

In order to make *ChemSep* as versatile as possible, we implemented the User Program entry under the "User program" option in the "Solve Options" menu. If you want to run your own program you can enter its full path and name (with the extension!) there and that program will be run no matter what kind of operation is selected. In order for a user program to have access to the SEP-file, the interface provides the user program with its name as the second commandline parameter. In case it also wants to use the temporary file, that is supplied as the third parameter. Running a user program will clear the screen before it starts executing the user program.

It is logical to suppose that the user just might want to run several programs or his own program(s) before/after calling *ChemSep*’s original calculation programs. To allow this you can use a batch file as the user program (use complete path, name and extension!). Look up in your DOS manual how to make batch files. In order to run the original calculations program we provide it to the batch file as the first commandline parameter and the SEP-file as the second. Even running the user program, the Interface generates a CHEMSEP.FIL file to be read by the calculation program. Here’s an example of such a batch file that will type the problem SEP-file first before running (note how the parameters are accessed with %1 and %2):

```bash
@Echo off
Rem -----------------------------------------------------------------------------
Rem Echo is set off to avoid to show this batch file is running
Rem use the "@" to suppress echoing of commands to the screen
Rem -----------------------------------------------------------------------------
Rem Type the SEP-file:
Rem -----------------------------------------------------------------------------
Type %2
Rem Pause for the user to strike a key:
Rem -----------------------------------------------------------------------------
Pause
Rem Run the appropriate ChemSep calculation:
Rem -----------------------------------------------------------------------------
%1
Rem Done!
```
Of course you can leave out all the Rem(arks) if you type this batch file but it is a good habit to document your code! You might create a complete set of batch files for different problems. Programs that might be run after the calculation might be cost estimation or design (in case of equilibrium simulation) programs. Using command line parameters (or the CHEMSEP.FIL file) your program might append its results to the SEP-file, so all results will be collected in there. Here is an example of a batch file that will automatically run ChemProp to generate physical property information in the sep-file:

```bash
@Echo off
echo Running ChemSep with physical property information generation
rem Run executable
   %1
rem Run ChemProp to generate physical property information
   c:\chemsep\bin\cp /c %2
rem Done!
```

The ultimate freedom is allowed by typing ”DODOS” as User Program in the Interface. The driver will automatically locate DOS and run it. All Dos commands will be available to you. The only way to access the SEP-file and other information is to read the CHEMSEP.FIL file. When you are ready to go back to the Interface you type ”EXIT” and press Enter.

By allowing you to shell to DOS or run batch files from within ChemSep we have created the maximum flexibility. Although ChemSep takes a lot of effort to prevent your system or ChemSep from crashing, it is possible to do so, using batch files or the DOS shell. Avoid deleting crucial files (such as executable files), or changing system parameters while the ChemSep-Driver is loaded. Do not load any TSR (Terminate and Stay Resident) programs or device drivers, since these programs will be removed from memory after the Driver takes over again. However, the interrupt to trigger these programs usually remains active. Changing directories is allowed, but remember the current CHEMSEP.FIL is written in the current directory! The driver will change the directory back to what it started running from, when returning to the Interface. If you want to change the current directory use the Directory option in the File menu! Do not load ChemSep again by invoking the driver, as multiple copies will be loaded into memory.

### 7.5 ChemSep Libraries and Other Files

A number of libraries has been added to the ChemSep package. We can divide the data libraries into the following groups:

- Pure Component Data (*.PCD)
- Interaction Parameter Data (*.IPD)
- Pure component LIBraries (*.LIB)
- Group Component Data (*.GCD)
- Internals Layout Data (*.ILD)
- Packing Data (CHEMSEP.*PD)
- Various ChemSep files (CHEMSEP.*)

The Pure Component Data (PCD) files contain the information of pure components like molecular weight, critical temperature, acentric factor, vapour pressure correlation constants, UNIFAC group ID's and number of groups etc. To access this data we have developed ChemLib which is a completely menu driven data manager - very similar to ChemSep, in fact - that will allow you to search PCD-file(s) and select component data records to edit. It can also move components from one PCD-file to another, or to text files. ChemSep v3.5 and higher can also use components from text files instead of PCD files. We prefer the faster (to search) binary PCD format for distribution, however, component data information in text format can have additional information as long as you append this information after the regular component's data items in the text file (ChemSep and ChemLib will stop reading after the fixed set of items and look for the start of the next component). The components ID numbers (Library Index) are based on the system developed at Penn State University and adopted by DIPPR.

The Interaction Parameter Data (IPD) files are ASCII text files with the interaction parameters for activity coefficient models and equations of state. Currently we have the following IPD files:

- NRTL.IPD
- UNIQUAC.IPD
- UNIQUACP.IPD (UNIQUAC Q' activity coefficient model)
- PR.IPD (Peng-Robinson EOS)
- SRK.IPD (Soave-Redlich-Kwong EOS)
- HAYDENO.IPD (Hayden O'Connell Virial EOS)

All these files are in plain text format file so the user can extend the data files (it is probably better to backup the original files or to use a new name for the extended files). Edit these files with any ASCII editor, or the built-in editor in ChemSep. The data in these files
comes after the line with the [IPD] keyword. The next line contains the file-comment after the "="", which will be used as a header in the interface. Next comes a line (only for activity coefficient models) with the interaction parameters units. Next comes the data, one line per binary pair. The first two numbers are the component library indices, then the interaction parameters. Appended text is optional but will also be displayed. As an example we include the first relevant lines of the NRTL/IPD file:

[IPD]
Comment=DECHEMA NRTL data @ 1atm.
Units=cal/mol
#
 1101  1921  -189.0469  792.8020  0.2999 Methanol/Water p61 1/1a

Lines starting with a "#" are comment lines which may appear anywhere. Since the interface will only start reading the file from the [IPD] keyword on, you can start the file with some text describing where the data was obtained and remarks on who/when/how changed the file. Most of the IPD files contain information from the DECHEMA series, a very extensive collection of interaction parameters. The Hayden O’Connell virial parameters are from Prausnitz et al. (1980).

Polynomial K-value and enthalpy correlation coefficients as well as extended Antoine coefficients are stored as component LIBraries (LIB files), which are ASCII files as well. The default LIB files are

- EANTOINE.LIB (Extended Antoine)
- H-POLY.LIB (Example polynomial enthalpy coefficients)
- K-POLY.LIB (Example polynomial K-value coefficients)

Here the interface starts reading the file after the [LIB] keyword. Again a comment is read from the next line (after the "=") and then the data starts with a line for each component (first the library index followed by the coefficients). For example the extended Antoine file (with data from Prausnitz et al., 1980) starts like:

[LIB]
Comment=Extended Antoine Prausnitz et al.
#
#  ID  A         B          C    D    E    F    G
  902 3.15799e+01 -3.2848e+2  0.0  0.0 -2.5980e+0  0.0  2.0  Hydrogen
Group Component Data (GCD) files are binary files containing data for group contribution methods such as UNIFAC or ASOG. Currently only UNIFAC files are present (UNIFACRQ.GCD, UNIFACVL.GCD and UNIFACLL.GCD) for Vapour-Liquid and Liquid-Liquid systems. These files need not be changed, unless for example the UNIFAC group tables have changed. Several GCD-files are used for the estimation of pure component data in ChemLib and UserPcd.

Internal layout data (ILD) files are text files which store tray or packing layouts for use by the nonequilibrium model. This way a specific design can be saved and reloaded upon demand.

Packing Data (CHEMSEP.*PD) files contain many physical and model parameters for various random and structured packings. They are text files that might be modified by the user with an ASCII editor, though there is one restriction, namely that the first line should not be changed! A shortened version of the structured packing data file CHEMSEP.SPD is shown below.

```plaintext
# CHEMSEP SPD Structured Packing Data
#
# Type (Name): Specific Equiv. Channel Packing Void ...
# packing diam. flow factor: fract: ...
#                     surface:      angle:
!-----------------------
Koch Flexipac 1    M   558/m 0.00897m 45   98/m 0.91 ...
Koch Flexipac 2    SS  223/m 0.01796m 45   43/m 0.95 ...
Koch Flexipac 3    M   135/m 0.03592m 45   26/m 0.96 ...
Koch Flexipac 4    M   69/m  0.07183m 45   20/m 0.98 ...
@-----------------------
Glitsch Gempak 1A   M   131/m 0.03592m 45   30/m  *   ...
Glitsch Gempak 2A   SS  223/m 0.01796m 45   52/m 0.95 ...
Glitsch Gempak 2AT  SS  223/m 0.01796m 45    *   0.96 ...
Glitsch Gempak 3A   M   394/m 0.01346m 45   69/m  *   ...
Glitsch Gempak 4A   M   525/m 0.00897m 45   105/m  *   ...
```

Lines starting with "#" are comment lines and are ignored (except for the first line). A line starting with "@" is used to set the length of the packing type identifiers which is set equal to the length of that line. Lines starting with an "@" will insert a separator in the list with packings and blank lines will be ignored. As you can see units may be added as long as there is no space between the number and the unitstring (otherwise errors will occur in reading this file!).

Miscellaneous ChemSep files include:
The CHEMSEP.UDF file contains the definitions for the units and the unit conversions in ChemSep. The first line must have the number of following lines with each a unit definition. Such a unit definition consists of 15 characters (from column 1) with the unit abbreviation (take care, these are case sensitive!) followed by 15 characters (from column 16) with the full unit name (not case sensitive). Then, from column 31 the offset-factor (fo) and multiplication factor (fm) come and finally the reference unit. The conversion is done according the following formula:

\[
\text{Number (in Reference units)} = \text{fm} \times (\text{Number (in Units)} - \text{fo})
\]

For example \(22\text{C} = 1.0(22 - 273.15) = 295.15\text{K}\). You can inspect ASCII text files with ChemSep's file viewer (F7) or make simple modifications with edit-file. However, we strongly suggest you do not change the original data files that come with ChemSep. We carefully selected and typed the data into these files and other users might use your changed data and obtain erroneous results. We urge you first to copy the file to another name before you change or add anything in these files. Errors in the unit conversion can be very frustrating so it is good to check some results if you have changed or added a unit definition. To encourage you to do so we made CHEMSEP.UDF a read-only file!

The CHEMSEP.SYN is a file containing synonyms for over 1000 compounds. While searching for a special component name you can use synonyms if you have selected to do so in the options interface spreadsheet. You must select this file as your synonyms file. The synonym search does not work while typing in a searchlist for a synonyms name. You will have to issue a search under the synonyms name! The synonyms file is an ASCII file you can modify to your needs.

The CHEMSEP.HLP file contains the information to provide you with help when you press (F1) for help. It is a binary file that can not be changed. It is generated with the MAKE-HELP utility from help source (HSR) files. This utility and the source files are not part of the ChemSep distribution. If you find errors or shortcomings in the help please notify the authors.
The CHEMSEP.TXT file contains the ASCII text of this book. Normally ChemSep will be configured with function key (F9) assigned to automatically load this file. There are also other formats available on our ftp-site (see Author information). The ASCII version is somewhat limited in available characters, sub- or superscripts, and equations.

The CHEMSEP.CNF file is used to store the default configuration, such as the macro definitions, directory structure, selected video and printer devices, and solve options. CHEMSEP.CNF is the default configuration file which will be loaded upon startup of the interface. If none is found in the current directory, the file supplied in the original distribution is used. This allows one to have multiple CHEMSEP.CNF files in different directories, which automatically configure the interface to (a) specific problem(s).

Finally, the CHEMSEP.SCR file contains the additional introduction screen(s) that are shown on startup of the program. These are used to stipulate conditions of the use of the program, but could be adapted to suit the users needs (for example if ChemSep is installed on a network, the operator can place important notes here). If the file contains more lines than can be shown on the screen, the user will have to press Enter multiple times to go through the various screens sequentially.

7.6 The SEP-file format

The SEP-files are written in a format which is readable by a human as well as by the calculation program. However, there are some strict rules! The SEP-file is constructed using delimiters in square brackets: [ ]. The order of the delimiters is not directly of importance (although ordering delimiters enhances the speed of reading a SEP-file). The sections under the delimiters are ordered and have a fixed format. Usually they consist of lines with a selected value and a comment. ChemSep uses two major sections: the INPUT and RESULTS sections. The INPUT starts with the delimiter [ChemSep] and ends with [End of Input]. The Results starts with [Results] and ends with [End of Results]. Within these sections there are sub sections. Note that a "*" denotes that the value is not yet set by the user. In some cases the Interface might create cryptic "* *" lines where the first star denotes the (not yet known) value of a selector and the second the description of the (not yet) selected item.

Remember that normally the Interface will not read any comments you have added yourself to the SEP-file and thus, not save them again when saving from within the Interface. To overcome this problem we have added the [User-Data] and [End User-Data] delimiters. When loading a SEP-file it is the last section that is looked for. If found, it is read into a buffer and written back to the file if saved again. Note that the delimiters each have to be on a separate line. You can use this data block to save information about the problem or to store parameters for your own programs that process SEP-files. You can edit User Data
within the interface of **ChemSep** under the Solve Options (**F6**). The following keywords are used to switch several hidden features (with explanation in "()":

[D-Models]
Diffusivity model (0=Maxwell-Stefan, 1=Effective)
Liquid MS-diffusivity model (0=Kooijman-Taylor, 1=Wesselingh-Krishna)

[No user interaction] (if present the user is not asked for more iterations if maximum number has been reached, but the program exits)

[Sensitivity] (sensitivity factors)
Vapour/Light-liquid Mass Transfer Coefficient
Liquid/Heavy-liquid Mass Transfer Coefficient
Interfacial Area

For a column problem the INPUT subsections are:

[CHEMSEP]
Version number and SEP file name

[Paths]
Current directories

[Units]
Current set of units

[Components]
Number of components, for each component library offset (in the PCD file), Index, Name, and PCD-library filename

[Operation]
Operation type and kind, condenser and reboiler types, number of stages, feeds, sidestreams, and pumparounds.

[Properties]
Property selections:

[Thermodynamics]
K model, Activity coefficient, Wilson model, UNIQUAC model, Equation of State, Cubic EOS, Virial EOS, Vapour pressure models
[Enthalpy]
Enthalpy model

[Physical Properties]
Physical Properties model selections

[Property Data]
Pure component data or interaction parameters if required

[Specifications]
Specifications:

[Heaters/Coolers]
Number and stage with duty, if specified.

[Sections]
Number and for each section: section number, begin and end stages, model selections, and tray/packing layout data.

[Efficiencies]
default efficiency, number of exceptions and stage with value, if specified.

[Pressures]
Type of pressure specification, condenser, top, bottom pressures, pressure drop.

[Heats]
Number and for each heat: state, stage, temperature, pressure, vapour fraction, number of component flows, molar component flows.

[SideStreams]
Number and for each side stream: stage, phase, specification type and value.

[Condenser]
Specification type and value(s) if present

[Reboiler]
Specification type and value(s) if present

[Solve options]
Initialization type, solving method, damping factor (if present), accuracy,
maximum number of iterations, and print options.

[Programs]
Temporary file, and user program

[User-Data]
Here the user data text is written.
[End User-Data]

[End of Input]

For an equilibrium column the [Sections] subsection will be absent, for a nonequilibrium model the [Efficiencies] subsection is not needed. For a flash a different set of specifications is present consisting of the [Feeds] subsection and a [Flash] specification subsection where flash type and specifications are made. The RESULTS section for a nonequilibrium problem looks like:

[Results]
[Profiles]
[Temperatures]
[Vapour phase compositions]
[Liquid phase compositions]
[Interface vapour mole fractions]
[Interface liquid mole fractions]
[Murphree efficiencies]
[Mass transfer rates]
[Condenser Heat Duty]
[Reboiler Heat Duty]
[K-values]
[Feed streams]
[Top product]
[Bottom product]
[Sidestreams]
[Designed Sections]
[Operating Limits]
[End of Results]

For equilibrium problems the Interface mole fractions, Murphree efficiencies, mass transfer rates, designed sections, and operating limits will be missing from the above list.
ChemSep supports dot matrix printers, laser printers, inktjet printers, or HP plotters to print/plot its graphs. Besides printing directly to a printer, ChemSep can also write the output to a file. ChemSep supports nine DeskTop Publishing (DTP) file formats as well. In order to print to a device or write to an output file ChemSep needs to know what type of device you have. Select device, mode, port (file) and work path (for temporary files written while generating output) in the printer setup under the graphs or the output setup in the options. Of course each printer has usually several different modes to print. By default none of the graphs are printed in color, unless a color device is selected. ChemSep lets you choose between three page formats:

- HALF-page portrait (7.2 inch * 4.67 inch),
- full-page LANDscape (9.56 inch * 7.2 inch), or
- FULL-page portrait (7.47 inch * 10 inch).

However, these page formats vary slightly from printer to printer. Plotters usually plot only at FULL size. Besides these three page formats there are (usually) additional modes. Select "Other" and type the mode number you want (see table below). The lowest mode number is zero and will always work.

ChemSep supports the following printers and plotters and desktop publishing file formats:

<table>
<thead>
<tr>
<th>Dot matrix printers:</th>
<th>Max.Mode</th>
<th>Desktop Publishing:</th>
<th>Max.Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epson 9-pin dot matrix</td>
<td>8</td>
<td>Zsoft PCX</td>
<td>1</td>
</tr>
<tr>
<td>Color Epson 9-pin dot matrix</td>
<td>5</td>
<td>Windows 3 BMP</td>
<td>1</td>
</tr>
<tr>
<td>Epson 24-pin dot matrix</td>
<td>8</td>
<td>Gem IMG</td>
<td>2</td>
</tr>
<tr>
<td>Color Epson 24-pin dot matrix</td>
<td>5</td>
<td>TIFF compressed</td>
<td>2</td>
</tr>
<tr>
<td>IBM Proprinter X24</td>
<td>8</td>
<td>TIFF uncompressed</td>
<td>2</td>
</tr>
<tr>
<td>IBM Quietwriter</td>
<td>8</td>
<td>ANSI CGM</td>
<td>1</td>
</tr>
<tr>
<td>Toshiba 24-pin dot matrix</td>
<td>2</td>
<td>AutoCad DXF</td>
<td>0</td>
</tr>
<tr>
<td>OkiData ML-92 dot matrix</td>
<td>2</td>
<td>Video Show</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Word Perfect Graphic</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Laser/Inktjet printers:</th>
<th>Max.Mode</th>
<th>Hewlett-Packard plotters:</th>
<th>Max.Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaserJet II</td>
<td>8</td>
<td>HP 7090</td>
<td>3</td>
</tr>
<tr>
<td>LaserJet III</td>
<td>8</td>
<td>HP 7470</td>
<td>1</td>
</tr>
<tr>
<td>DeskJet</td>
<td>8</td>
<td>HP 7475</td>
<td>7</td>
</tr>
<tr>
<td>Color DeskJet</td>
<td>8</td>
<td>HP 7550</td>
<td>7</td>
</tr>
<tr>
<td>PaintJet</td>
<td>14</td>
<td>HP 7585</td>
<td>9</td>
</tr>
<tr>
<td>Postscript</td>
<td>11</td>
<td>HP 7595</td>
<td>9</td>
</tr>
</tbody>
</table>
Table 7.1: Interface Assigned Types

<table>
<thead>
<tr>
<th>Operation</th>
<th>Internal Type</th>
<th>Model Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor-Liquid (VL)</td>
<td>Discrete (DIT)</td>
<td>Mass transfer coefficient (MTC)</td>
</tr>
<tr>
<td>Liquid-Liquid (LL)</td>
<td>Continuous (CIT)</td>
<td>Pressure drop (PD)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vapor flow (VF)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquid flow (LF)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Entrainment (Entr)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Holdup (Hold)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Light liquid flow (LLF)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Heavy liquid flow (HLF)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Backmixing (Back)</td>
</tr>
</tbody>
</table>

7.8 Model Definition and Selection

ChemSep reads a definitions file (CHEMSEP.DEF) at startup, where models for the mass transfer coefficients, pressure drop, flow models, entrainment, and holdup are defined. This alleviates us from adapting the ChemSep interface upon any addition or modification of a model. In case no definitions file is found, the nonequilibrium part of ChemSep is disabled. The definitions file must start with "[ChemSep Definitions]" followed by a Version field (like "Version=1.00"). Lines that start with "#" are comment lines. Five different definitions are in the file: [InternalType], [Operation], [ModelType], [Internal], and [Model]. Each of these has the following fields: ID, Name, and Short, for example:

[Operation]
ID=1
Name=Vapor-Liquid
Short=VL

The five different types of definitions may be mixed throughout the definitions file. The [Internal] definitions also contain the fields: Type, Operation, Models, and Parameters. The [Model] definitions also contain the fields: Type, Operation, Internals, and Parameters. Short fields are optional, and have a maximum length of ten characters, used for displaying selected models etc. ID fields associate a unique number to the definition. Only for the internal and model definitions non-unique numbers are allowed. When the interface reads the definitions file it uses the Short descriptions to assign the ID's for the Operations, InternalTypes and ModelTypes, see Table 7.1 (the Short descriptions used by the interface are in parenthesis). Thus, you will have to use these Short descriptions but are free to change the ID numbers or names. The [Models] field of an internal definition defines all the models that need to be selected for this internal. Either ID numbers or short notation may be used,
### Table 7.2: Assigned Internals and Vapor flow, Liquid flow, and Entrainment Models

<table>
<thead>
<tr>
<th>Internal</th>
<th>Vapor Flow / Light liquid flow</th>
<th>Liquid Flow / Heavy liquid flow</th>
<th>Entrainment / Backmixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble cap tray (1)</td>
<td>Mixed (1)</td>
<td>Mixed (1)</td>
<td>None (1)</td>
</tr>
<tr>
<td>Sieve tray (2)</td>
<td>Plug flow (2)</td>
<td>Plug flow (2)</td>
<td>Estimated (2)</td>
</tr>
<tr>
<td>Valve tray (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dumped packing (4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structured packing (5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium stage (6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RDC compartment (7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spray column stage (8)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

as long as they are defined ModelTypes. The internal type is a defined InternalType, the internal operation a defined Operation. The optional Parameters field contains the names of parameters that are required by the model (this is currently not yet implemented). For example, the definition of the bubble cap tray internal is:

```plaintext
[Internal]
ID=1
Name=Bubble cap tray
Type=Discrete
Short=Bubble cap
Operation=VL
Models=MTC,PD,VF,LF,Entr
```

The assigned internal types for the ChemSep Interface are listed in Table 7.2. This table also lists defined vapor and liquid flow models and models for entrainment. An example of a model definitions is:

```plaintext
[Model]
ID=1
Name=AIChE
Type=MTC
Operation=VL
Internals=Bubble cap,Sieve tray,Valve tray
```

Assigned models for Mass Transfer Coefficient and Pressure Drop models are listed in Table 7.3. Model parameters may be read from parameter libraries (*.PAR) that have a format like the packing data files. The first line of such a ASCII text file must start with ";#
**Table 7.3: Assigned MTC and PD Models**

<table>
<thead>
<tr>
<th>Mass Transfer Coefficient</th>
<th>Pressure Drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIChE (1)</td>
<td>Fixed (1)</td>
</tr>
<tr>
<td>Chan Fair (2)</td>
<td>Estimated (2)</td>
</tr>
<tr>
<td>Zuiderweg (3)</td>
<td>Ludwig 1979 (3)</td>
</tr>
<tr>
<td>Hughmark (4)</td>
<td>Leva GPDC (4)</td>
</tr>
<tr>
<td>Harris (5)</td>
<td>Billet-Schultes 1992 (5)</td>
</tr>
<tr>
<td>Onda et al. 1968 (6)</td>
<td>Bravo-Rocha-Fair 1986 (6)</td>
</tr>
<tr>
<td>Bravo-Fair 1982 (7)</td>
<td>Stichlmair-Bravo-Fair 1989 (7)</td>
</tr>
<tr>
<td>Bubble-Jet (9)</td>
<td></td>
</tr>
<tr>
<td>Bravo-Rocha-Fair 1992 (10)</td>
<td></td>
</tr>
<tr>
<td>Billet-Schultes 1992 (11)</td>
<td></td>
</tr>
<tr>
<td>Nawrocki et al. 1991 (12)</td>
<td></td>
</tr>
<tr>
<td>Chen-Chuang (13)</td>
<td></td>
</tr>
<tr>
<td>Handlos-Baron-Treybal (14)</td>
<td></td>
</tr>
<tr>
<td>Seibert-Fair (15)</td>
<td></td>
</tr>
<tr>
<td>Kronig-Brink-Rowe (16)</td>
<td></td>
</tr>
<tr>
<td>Rose-Kintner-Garner-Tayeban (17)</td>
<td></td>
</tr>
<tr>
<td>Sherwood (20)</td>
<td></td>
</tr>
</tbody>
</table>

CHEMSEP xxxx” where xxxx must be replaced by the full name of the model (as defined in CHEMSEP.DEF). Upon choosing the library option in the interface the library will be automatically pre-selected if the name of the library file is the same as the short name of its model.

### 7.9 Author and program information

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We typed most of the code with the Multi-Edit text editor. It allows us to switch between the source code of the drivers, interfaces, and column simulation executables, as well as the text files for the help and documentation. Each different type of file has its own commands associated with it (compile source code, run latex on the documentation, etc.). As the project is over several hundred thousands lines of source and text, the editor has proven to be very valuable to us.

The drivers and interfaces are written in Turbo Pascal (version 7.0), the column and flash programs are written in standard Fortran 77, which we compile with WATCOM Fortran and link with the CauseWay DOS extender. The source code for the simulation executables has also been successfully compiled and executed on a range of operating systems and platforms.

Acknowledgements

WordPerfect is a product of the WordPerfect Corporation. Microsoft Word is a product of Microsoft Incorporated. DOS4GW is a product of Rational. CauseWay is a product of Devore software Incorporated. Multi-Edit is a product of American Cybernetics. WATCOM F77 is a product of WATCOM Incorporated. Turbo Pascal is a product of Borland International Incorporated.

References

Chapter 8

FlowSheeting

By combining different ChemSep models you can actually simulate (small) flowsheets. Several other common unit operations (reactor, make-up stream, and stream splitter) are available to make this possible. Simulating flowsheets with the utility program fs is illustrated with several examples in this chapter.

8.1 Flowsheet Input File

The flowsheet utility uses a text file as input. You will have to make this file yourself (with, for example, the edit option in ChemSep’s file menu). The ChemSep distribution contains various examples (in the fs directory). To explain the format of this file we will use an example where we simulate the production of diethylether from an ethanol-water (85%-15%) feed, as shown in Figure 8.1. The conversion of the ethanol in the reactor is only 50% and the unreacted ethanol has to be recycled. Pure ether (99.5%) and water (with 1% ethanol) are the products. The reaction is:

\[ 2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \]  

(8.1)

In the flowsheet input file (ep.fs) you define the units and streams in your flowsheet. The input file consists of four parts. The first part consists of one section where all the components, units, streams, feeds, and stream estimates are declared as well as the output file, executable directory, and the method and accuracy used in solving the flowsheet.

[Flowsheet]
Comment=Ethylether Production
Components=Water, Ethanol, Diethylether
Units=Mixer, Reactor, Sep-1, Sep-2
Figure 8.1: Diethylether Production
Streams=1,2,3,4,5,6,7,8
Feeds=1
Estimates=7
Output=ep.fs
ExeDir=c:\cs\exes\nMaxIter=20
Method=Direct
Accuracy=0.001

! this is a comment

The section starts with the [Flowsheet] identifier. The next lines are part of this section until an empty line is found. You can add (non empty) comment lines in the input file by, for example, using any punctuation character to start the line. The flowsheet program looks for the specific keywords and if none is found it regards the line as a comment. However, comment lines do not get copied to the output file. In each section the keywords can be different. The keywords are the identifiers left of the equal signs in the above flowsheet section. They are not case-sensitive and you may enter them in any order (some restrictions do apply, though).

Comma’s are used to separate the various components, streams, units, feeds, or stream estimates (therefore, they can not be part of a name. This is important as IUPAC component names sometimes use comma’s. In that case omit the comma’s in the component name. Currently the component names are not checked and it is assumed that the same components in the same order are used in all the units! This is very important. The case of the names you specify is not important but the one used in the flowsheet section is used in the rest of the report.

In our example we have the following streams we have given our streams numbers from 1 to 8 (instead of numbers names may also be used). We have only one feed, 1, and we will make a stream estimate for the recycle (7). Stream 2 is a stream that is not used (we need it since the flash program that simulates the mixer produces a vapor product stream which we have to assign). Our unit operations are a mixer, reactor, and two columns (Sep-1 and Sep-2) where we separate the products. Our output file is ep.fs (the same name as our input file which will be overwritten) and the flowsheet method is Direct substitution with a convergence criterion of 0.001. The maximum number of iterations is specified here as 20.

The next part describes the units and, therefore, can consist of multiple sections. We have four units in our example. Each unit section starts with the [Unit] identifier and has five keywords: Name, File, Type, Inlets, and Outlets.

[Unit]
Name=Mixer
File=ep-mix.sep
Type=4g-flash.exe
Inlets=1,7
Outlets=2,3

[Unit]
Name=Reactor
File=ep-reac.sep
Type=reactors.exe
Inlets=3
Outlets=4

[Unit]
Name=Sep-1
File=ep-sep1.sep
Type=4g-neq2.exe
Inlets=4
Outlets=5,6

[Unit]
Name=Sep-2
File=ep-sep2.sep
Type=4g-neq2.exe
Inlets=6
Outlets=7,8

The specified unit name must match the one given in the flowsheet section. The unit file is the associated data file, for most units it is the Sep-file which was generated by ChemSep. The unit type is the program that must be run to simulate this specific unit. For a ChemSep flash that is 4g-flash.exe, for an equilibrium column 4g-col2.exe, and for a nonequilibrium column 4g-neq2.exe. This allows you to make your own unit simulation program that reads a datafile with feed and product section as in a Sep-file. In the case of the reactor this is done by the reactors.exe program (which is described below).

The units are connected by in- and outlets streams, which were declared in the flowsheet section above. Be sure to use the same names (case is not important) as otherwise the flowsheet will be incorrect or incomplete. If you just want to analyze a flowsheet or not to simulate the unit it, omit the unit file and type (they will not be executed).

[Feed]
Name=1
Temperature=40C
Pressure=1.01325bar
Rate=20mol/s
The next part consists of the [Feed] sections where the feed streams are defined. The specified feed name must match the one given in the flowsheet section (again, case is not important). Furthermore, the feed stream pressure, temperature, flowrate, and composition must be specified. Append units when specifying temperatures, pressures, and flows. The default units (which can be omitted) are temperatures in degrees Celsius, pressure in bar (absolute), and flows in mol per second. The flowrate and compositions can also be set by specifying the component flows, for example for the definition of the feed above we could use as well

```
[Feed]
Name=Feed
Temperature=40C
Pressure=1atm
F=3.17
```

where F is the list of component flows (default units mol/s). If all the component flows are specified, the total flowrate and compositions are computed. A partial list (like Z=*,0.85) can be specified as well, which is useful for supplying stream estimates.

All streams are reset at the start, and when the inlets are written to the unit-file only the specifications supplied in the input file are written to the unit file. If stream values are reset the values already present in the unit file will be used.

The last part consists of [Estimate] sections where estimates of stream variables (flow, temperature, pressure, or composition) can defined. This part is optional and only required if you specified streams under the estimates keyword in the flowsheet section. Stream estimates have the same input format as feeds have, except for the different identifier, of course. In our case we estimate the recycle stream 7 to start with a better value of the flowrate to the reactor:

```
[Estimate]
Name=7
Temperature=80C
Pressure=1.01325bar
Rate=10mol/s
Z=0.85,0.15,0
```

The files that make up our example all start with EP (ep.fs, ep-mix.sep, ep-reac.sep, ep-sep1.sep, ep-sep2.sep) and are included in the ChemSep distribution (in the fs directory).
8.2 Flowsheet execution

If the flowsheet input is correct the flowsheet program starts the execution of each units program with the specified file written to the \textbf{ChemSep.Fil} file in the default directory (\textbf{ChemSep} programs read this file to obtain the Sep-file to simulate). The order of execution is the order as was specified in the flowsheet section (so you can manipulate it). If a unit file or type is missing execution of that unit is skipped.

A unit evaluation takes the unit inlet streams and puts them (in the same order!) into the file under the [\textbf{Feeds}] section. Then it runs the associated program and reads the [\textbf{Top product}] section as the first outlet stream, the [\textbf{Bottom product}] section as the second outlet stream, and each following [\textbf{Sidestream} section as the third, fourth, etc. outlet streams.

In the case that the flowsheet analysis finds one or more cycles it will inform you and set the recycle flag to start an iterative run. The criterium is the maximum relative (or absolute) differences in stream variables when any stream gets updated. For each iteration this is initially set to zero and computed over the simulation of all the units. Convergence is obtained if the criterium is below the specified accuracy (default is $10^{-2}$) or if the maximum number of iterations (default is 20) is attained (In the case that an absolute criterium is used the temperature difference is divided by 10 and for the pressure by $10^4$ to scale the differences).

Sometimes it may be handy to abort the simulation or to stop it and inspect certain streams during the simulation. This can be accomplished by holding the \textbf{Shift} keys or toggling \textbf{Caps Lock} on. The program will beep and display the next unit to be simulated, the current attained convergence, and the current iteration number. A simple menu allows you to change the maximum number of iterations or the accuracy, display a stream, continue, or to quit the simulation. It will also allow you to swap to DOS to do other work, like loading Sep-files into the \textbf{ChemSep} interface to make changes or to evaluate the intermediate results. Typing "exit" will then return you to the flowsheet program (don't forget this).

Once the flowsheet is converged the output file is written, consisting of four parts: the input file (generated from the information read in), a flowsheet analysis, the mass balances, and a report of all the streams.

8.3 Flowsheet Analysis

The flowsheet analysis of our depropanizer example is rather simple. Flowsheet reports the incidence, adjacency, distance, and cycle matrices for the specified flowsheet.
Incidence Matrix  
------------------
Unit\Flow:  1  2  3  4  5  6  7  8
Mixer       +  -  -  +
Reactor     +  -  
Sep-1       +  -  -
Sep-2       +  -  -

Adjacency Matrix  
------------------
Unit:       Mixer Reactor Sep-1 Sep-2
Mixer       3
Reactor     4
Sep-1       6
Sep-2       7

Distance Matrix  
------------------
Unit:       Mixer Reactor Sep-1 Sep-2
Mixer       4  1  2  3
Reactor     3  4  1  2
Sep-1       2  3  4  1
Sep-2       1  2  3  4

Cycle Matrix  
--------------
Cycle: Rank: Streams:
C1  4  3,4,6,7

Stream: Frequency:
3  1
4  1
6  1
7  1

Cycle: Rank: Units:
C1  4  Mixer, Reactor, Sep-1, Sep-2

Evaluation order from analysis = Reactor Mixer, Sep-1, Sep-2

These matrices can be useful in assessing the structure of the flowsheet and the evaluation order of the units. The flowsheet analysis will also give an ordering of the units that might be better than the specified order.
8.4 Convergence

This short section displays whether the flowsheet was converged and, if iteration was required, the attained convergence criterion and number of iterations.

Flowsheet is solved.
Attained convergence = 0.000826326
Number of iterations = 10
Used relative differences.

8.5 Mass Balances

In the balances section total mass balance is given for each unit, and for the overall flowsheet. If a flowsheet is converged, each balance should equal zero or some small number (relative to the in- and outlet flows of the specific unit). The balances are first written as the names of the units and associated streams, then in the total molar flowrates:

Balances in mol/s

Total Molar Balances:
Mixer = 1+7-2-3 = 20+19.7097-0-39.694 = 0.0157021
Reactor = 3-4 = 39.694-39.694 = 0
Sep-1 = 4-5-6 = 39.694-8.45862-31.2354 = -0.0000204891
Sep-2 = 6-7-8 = 31.2354-19.7097-11.5257 = 0
Overall = 1-2-5-8 = 20-0-8.45862-11.5257 = 0.0156797

Water Balances:
Mixer = 3+2.799822-0-5.797864 = 0.00195764
Reactor = 5.797864-14.21037 = -8.412508
Sep-1 = 14.21037-0.0000697587-14.21033 = -0.0000232831
Sep-2 = 14.21033-2.799822-11.41044 = 0.0000614673

Ethanol Balances:
Mixer = 17+16.66376-0-33.65003 = 0.0137314
Reactor = 33.65003-16.82501 = 16.82502
Sep-1 = 16.82501-0.0460432-16.77897 = 0
Sep-2 = 16.77897-16.66376-0.115257 = -0.0000505315

Diethylether Balances:
Mixer = 0+0.246113-0-0.246111 = 1.920853E-06
Reactor = 0.246111 - 8.658619 = -8.412507
Sep-1 = 8.658619 - 8.412504 - 0.246113 = 1.949957E-06
Sep-2 = 0.246113 - 0.246113 - 3.203753E-08 = -3.203753E-08

Care must be taken that the individual component balances are also satisfied, they are written after the total molar balances. Also, a reactor total molar balance will not be zero if the reaction changes the number of moles in the mixture. A reactor component balance will not be zero if that component is involved in one of the reactions that has a nonzero conversion. In the case of our example we see that the reaction rate is 8.4 mol/s diethylether.

### 8.6 Stream Report

The stream report lists the streams after the execution has stopped.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Temperature (C)</th>
<th>Pressure (bar)</th>
<th>Flowrate (mol/s)</th>
<th>Zwater</th>
<th>Zethanol</th>
<th>Zdiethylether</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>1.01325</td>
<td>20</td>
<td>0.15</td>
<td>0.85</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>58.68402</td>
<td>1.01325</td>
<td>39.694</td>
<td>0.146064</td>
<td>0.847736</td>
<td>0.00620021</td>
</tr>
<tr>
<td>4</td>
<td>49.85001</td>
<td>1.01325</td>
<td>39.694</td>
<td>0.357998</td>
<td>0.423868</td>
<td>0.218134</td>
</tr>
<tr>
<td>Stream</td>
<td>Temperature (°C)</td>
<td>Pressure (bar)</td>
<td>Flowrate (mol/s)</td>
<td>Zwater</td>
<td>Zethanol</td>
<td>Zdiethylether</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------</td>
<td>---------------</td>
<td>-----------------</td>
<td>--------</td>
<td>----------</td>
<td>--------------</td>
</tr>
<tr>
<td>5</td>
<td>34.76102</td>
<td>1.01325</td>
<td>8.45862</td>
<td>8.24705E-06</td>
<td>0.00544335</td>
<td>0.994548</td>
</tr>
<tr>
<td>6</td>
<td>77.918</td>
<td>1.01325</td>
<td>31.2354</td>
<td>0.454943</td>
<td>0.537178</td>
<td>0.0078793</td>
</tr>
<tr>
<td>7</td>
<td>76.11902</td>
<td>1.01325</td>
<td>19.7097</td>
<td>0.142053</td>
<td>0.84546</td>
<td>0.0124869</td>
</tr>
<tr>
<td>8</td>
<td>96.62302</td>
<td>1.01325</td>
<td>11.5257</td>
<td>0.99</td>
<td>0.01</td>
<td>2.77966E-09</td>
</tr>
</tbody>
</table>

### 8.7 Commandline Options

The flowsheet program has several options which can be specified on the commandline when you start it. These are described below in some examples followed by explanation (after the equal).

- **\x** = Skip execution
- **\r** = Force iteration
Although the streams in the input file can be defined by any units, the output file will be written with the default units (including the part with the input file!). Unit definitions are read from the FS.UDF file, or if that file is not found, from the CHEMSEP.UDF file.

8.8 Other Unit Operations

If you want to simulate a complex flowsheet you need several other unit operations models besides flash and column operations. The flash unit can also be used to model heaters, coolers, or pumps. However, a nonsense stream has to be added as most streams are either a vapor or liquid. Here we discuss several other unit operations which are commonly used in flowsheets. They have their own little programs for which we supply the pascal code (to be compiled with Borland Pascal, v7 or later). Most of them are limited to only a couple of hundred lines which mostly cover the in- and output. If you require other unit operations you could code them yourself (we welcome your pascal code for unit operations to enhance the flowsheet capabilities).

8.8.1 Simple Reactor

A unit operation used in almost any flowsheet simulating a chemical plant is the reactor. We have implemented a simple reactor model which can handle multiple reactions with specified conversion(s). The conversion is adapted in case one of the component flows is constraining. The input file has a similar style as that of the sep-files and flowsheet input file. The reactor specifications (conversion, outlet temperature, pressure drop, and the reaction stoichiometry) are given under the [Reactor] section which is followed by a [Feeds] section following the sep-file format (only one feed is allowed). The first line in the [Reactor] section contains the reactor’s name, followed by the outlet temperature, pressure drop, number of components, and number of reactions. Then, for each reaction, lines for the base component, the conversion based on the base component feed/flow, and the reaction’s stoichiometry coefficients (coefficients for each component; negative for reactants, positive for products).

Production of benzene by hydrogenation of toluene

----------------------------------------------------------------------------
Reactions:
\[ \text{C}_5\text{H}_5\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{C}_6\text{H}_6 \]
\[ 2 \text{C}_5\text{H}_5\text{CH}_3 + \text{H}_2 \rightarrow 2 \text{CH}_4 + (\text{C}_5\text{H}_5)_2 \]

Components:
Toluene, Hydrogen, Methane, Benzene, Diphenyl

[Reactor]
Benzene-Reactor
400 K outlet temperature
10000 Pa pressure drop
5 components
2 reactions
1 base component r1
0.9 conversion r1
\(-1\ -1\ 1\ 1\ 0\) stoichiometry coef. r1
1 base component r2
0.2 conversion r2
\(-2\ -1\ 2\ 0\ 1\) stoichiometry coef. r2

[Feeds]
1 number
*
*
400 K temperature
101325 Pa pressure
*
5 components
0.1 kmol/s toluene
0.1 kmol/s hydrogen
0 kmol/s methane
0 kmol/s benzene
0 kmol/s diphenyl

After running the reactors program the output is written to the same file and contains a small [Results] section which reports whether the specified convergence(s) was attained followed by a [Top product] section with the reactors outlet stream.

[Results]
Conversion(s) on base components was limited by component 1 to 90% of specified conversion(s)
If there are multiple reactions and one (or more) of the component feedflows is constraining the reactions, the conversions are all equally affected. For the ether reactor of our example the reactors input file looks like:

```
[Reactor]
Reactor
323 K outlet temperature
0 Pa pressure drop
3 components
1 reactions
2 base component r1
0.5 conversion r1
1 -2 1 stoichiometry coef. r1

[Feeds]
1 Number
1 Feed state T & P
*
331.834 Temperature
101325 Pressure
* Vapour fraction
3 component flows
0.00579786 Component 1 flow
0.03365 Component 2 flow
0.000246111 Component 3 flow
```

### 8.8.2 Make-Up Feeds

Often, when a flowsheet contains a recycled solvent or base material, a (small) make-up feed is required. Since the exact flowrate of the make-up feed is unknown, we made a unit operation that will add a make-up feed (the first feed) to another stream (the second feed) to obtain a specified total flowrate.

```
[Make-up]
Make-up Unit
.06 Total flowrate (always in kmol/s)

[Feeds]
2 Number
1 Feed state T & P
1 stage
When the make-up program runs it appends a small [Results] section displays the total flowrate of the make-up feed followed by a [Top product] section containing the resulting stream.

[Results]
0.0001649 = Make-up flow

Since the make-up feed has to be specified at the beginning this could cause the mass balances to be incorrect. Therefore, if the flowsheet encounters a make-up unit, and the first inlet stream is declared as a feed, its flowrate is adapted on writing the output.

8.8.3 Stream Splitter

Similarly to the Make-up unit, flowsheets containing recycles sometimes need to purge some part of the recycle to prevent build-up of various components in the cycle. This means that the recycle stream must be split into two parts. The splits program implements the stream split operation. The input file for the splitter consists of a [Splitter] section, containing the name of the unit and a splitfactor (which can range from zero to unity):

[Splitter]
Recycle purger
0.1
This is followed by the regular \textbf{Feeds} section (see for example, the reactor description), where only one feed may be specified. After running the \texttt{splits} program top and bottom product streams will be appended to the input file, where the top product stream has a flowrate equal to the feedflowrate multiplied with the splitfactor, and the bottom product contains the rest of the feedflow.

### 8.9 Examples

Here we discuss several examples which have been run with the flowsheet program. We will not supply all the details as they can be found in the various files that are distributed with ChemSep. Note that all these examples can be solved using the nonequilibrium column models.

#### 8.9.1 Extractive Distillation (PH)

We need to separate an equimolar mixture of methylcyclohexane (MCH) and toluene, and do this by extractive distillation with phenol as solvent. The flowsheet is shown in Figure 8.2. Valve trays are used for both the columns using the design mode nonequilibrium simulator. The Phenol recycle is cooled to 100 $^\circ$C. For a high purity of the products the solvent feed to MCH/Toluene feed ratio as well as the reflux ratio need to be sufficiently high (for the extractive column).

#### 8.9.2 Distillation with a Heterogeneous Azeotrope (BW)

Water and butanol form an azeotrope, so that they cannot be separated by conventional distillation. However, at not too high temperature, they form two liquid phases; an aqueous phase with little butanol and a butanol phase with a large mole fraction of water. We can use a decanter to separate the two liquid phases. A feed which is predominantly water but contaminated with butanol (1 mole\%) can be separated into two pure products using such a decanter. The flowsheet is shown in Figure 8.3. The first column produces a water bottom product, and the vapor is fed to a condenser/cooler and then to the decanter. There we obtain a water- and a butanol-rich stream which get recycled to the columns. In a second column we can then produce butanol as the butanol-rich recycle contains much more butanol than the butanol-water azeotrope.
Figure 8.2: Extractive Distillation
Figure 8.3: Distillation with Decanter
8.9.3 Distillation of a Pressure Sensitive Azeotrope (MA)

Methanol and acetone form also an azeotrope. However, the composition of the azeotrope is sensitive to the pressure. We can make use of this to separate the two components into pure products by operating two columns at different pressures to change the azeotrope composition. The separation of an equimolar feed of methanol and acetone is shown in Figure 8.4. This type of azeotropic distillation is rare as the azeotrope composition needs to be quite sensitive to the pressure in order to obtain a recycle stream which is not unreasonably large, and that the pressures are such that no special columns or equipment is required.

8.9.4 Petyluk Columns (PETYLUK)

To lower the energy consumption of separation trains, two columns separating 3 components can be replaced by one column with a condenser and reboiler plus one column without condenser and reboiler. The feed is fed to this (first) column, which receives a vapor to the bottom and a liquid at the top from the (second) column with the condenser and reboiler. In turn, the products of the first column are fed into the second column at the sidestream stages. Figure 8.5 shows such a configuration for the separations of three alcohols. To get this flowsheet to run requires that you can solve both the columns separately, which is not easy. The second column needed some specific user initialization information to run. Afterwards convergence can be obtained more easily by using the old results as initialization.

8.9.5 Extraction with Solvent Recovery (BP)

Extraction can be used to separate aromatics from paraffins. This is a common type of separation in the crude oil refining. A simplified example is shown here where we separate benzene from n-pentane, using an extraction with sulfolane as solvent. The extractor is a rotating disk contactor (RDC) operating at 50°C. The solvent is recovered from the extract by "ordinary" distillation. UNIQUAC parameters for the components are given in Table 8.1. The extraction is dependent on the temperature as can be seen from the interaction parameters, which can be used to manipulate the separation. See Figure 8.6 for the flowsheet.
Figure 8.4: Azeotropic Distillation at Two Pressures
Figure 8.5: Petyluk Columns
Figure 8.6: Extraction with Solvent Recovery
Table 8.1: UNIQUAC LLE interaction parameters (K)

<table>
<thead>
<tr>
<th>Components i-j</th>
<th>25°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_{ij}$</td>
<td>$A_{ji}$</td>
</tr>
<tr>
<td>pentane-benzene</td>
<td>295.38</td>
<td>-171.63</td>
</tr>
<tr>
<td>pentane-sulfolane</td>
<td>532.04</td>
<td>187.84</td>
</tr>
<tr>
<td>benzene-sulfolane</td>
<td>151.02</td>
<td>-36.08</td>
</tr>
<tr>
<td>pentane-benzene</td>
<td>179.86</td>
<td>-95.70</td>
</tr>
<tr>
<td>pentane-sulfolane</td>
<td>375.93</td>
<td>247.77</td>
</tr>
<tr>
<td>benzene-sulfolane</td>
<td>131.51</td>
<td>-6.28</td>
</tr>
</tbody>
</table>
Chapter 9

ChemProp

In this chapter we will briefly discuss ChemProp which allows us to obtain physical property predictions in an interactive manner.

9.1 Input

ChemProp requires you to select the components in the mixture just like ChemSep. Under conditions the pressure, temperature, and overall compositions need to be specified, similarly to the feed specifications for a distillation column in ChemSep. The phase equilibrium determines the type of equilibrium calculation. If set to none, no phase equilibrium calculations are done. If set to VLE then vapor and liquid equilibrium is calculated. The vapor and liquid properties are calculated given the compositions from the phase calculations. If a phase is absent, no physical properties are calculated. Under properties the selection of the thermodynamic and physical property models needs to be made. If data is required for the selected models this is also entered here. This selection of models is identical to that in ChemSep.

9.2 Results

9.2.1 Component properties

The component properties table displays the pure component data for all the components. The properties that are temperature dependent are evaluated at the specified temperature under the conditions. You can press F8 to change the conditions, and F9 to change the


9.2.2 Mixture properties

The mixture properties table displays the mixture physical properties, such as densities, viscosities, heat capacity, thermal conductivity, and surface tension. If specified, a flash calculation is calculated to determine the phase compositions. Then the properties are calculated for each of the existing phases at the phase compositions. If no phase equilibrium is calculated the mixture physical properties are calculated for both phases at the overall compositions as specified in the conditions. You can press F8 to change the conditions, and F9 to change the models.

9.2.3 Tables

The table option displays a specific property, or a set of properties, as function of a temperature, pressure, or composition range. The number of points can be set as well as the range limits. You can press F8 to change the conditions, and F9 to change the models.

9.2.4 Graphs

The graph option displays the same information as in the table option but in graphical form. If multiple properties were specified the user must select which axis is to be used for displaying each property. You can press F8 to change the conditions, and F9 to change the models.

9.2.5 Phase diagrams

Binary and ternary phase diagrams are supported. Constant temperature (Pxy) or pressure (Txy) binary diagrams can be drawn, or XY diagrams at constant pressure or temperature. A three dimensional TPxy diagram can also be drawn where the user can specify sets of temperatures and pressures where XY diagrams are to be calculated and drawn.

For the ternary diagrams only the diagrams at constant pressure (Txy) and pressure (Pxy) are available. For these diagrams the residu curve maps can be calculated. In these ternary diagrams, residu curves can be drawn on the bubble temperature surfaces, as well as their projections on the bottom of the ternary diagram. The number of residu curves can be specified.
9.2.6 Diffusivities

Liquid and vapor Maxwell-Stefan as well as Fick diffusivities can be drawn. Also the inverse B matrix and Gamma matrix can be drawn for a ternary mixture. Temperature and pressure can be specified, or the temperature can be calculated from the phase equilibrium. The number of lines in the figure determines the detail in the surfaces that is visible.

9.3 Various

Miscellaneous ChemProp files include:

- CHEMPROP.UDF: Units Definition File
- CHEMPROP.HLP: HeLP file
- CHEMPROP.CNF: the default CoNfiguration file
- CHEMPROP.SCR: the additional introduction SCReen(s)
Chapter 10

ChemLib

This chapter discusses the pure component data librarian and the format of the binary and text Pure Component Data files. ChemSep and ChemProp need these component data to calculate the required thermodynamic and physical properties. Therefore, they are an essential part in the package. Extending the supplied libraries (or making your own) is necessary when you want to use components that are not part of the standard library.

10.1 Pure Component Data files

Two types of PCD files can be used: binary and text. The binary files were initially used to facilitate fast lookup and searching of component data. With today’s bigger hard disks and faster machines, the reasons for using binary files have diminished. However, the standard libraries are in binary read-only format as it makes it more difficult to make changes to the library. This reduces the chance a user’s problem is caused by bad modifications of the standard PCD library.

However, the ChemSep interface and calculation programs can also handle component data files in text format. The USERPCCD program used to generate this type of files to allow users to add their own components to ChemSep. With the inclusion of ChemLib this has become easier and USERPCCD is no longer supplied. ChemLib can edit binary PCD files and export/import to and from text format component data files.

For a proper functioning of the models in ChemSep it is pertinent that the correct component data is used. Inspection of the component data used in any simulation is highly recommended. That is why there is a special link to the ChemLib program in the ChemSep interface (at the bottom of the input menu). This section we will describe the types of data in the PCD files and their typical usages.
10.1.1 Name and library index

We have adopted the same component names as used by DIPPR (as DIPPR is becoming an industry standard). The components ID numbers (Library Index) are based on the system developed at Penn State University (also adopted by DIPPR). Some common used components ID numbers are:

<table>
<thead>
<tr>
<th>Component</th>
<th>ID</th>
<th>Name</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1</td>
<td>Water</td>
<td>1921</td>
</tr>
<tr>
<td>Ethane</td>
<td>2</td>
<td>Chloroform</td>
<td>1521</td>
</tr>
<tr>
<td>Propane</td>
<td>3</td>
<td>Methanol</td>
<td>1101</td>
</tr>
<tr>
<td>i-Butane</td>
<td>4</td>
<td>Ethanol</td>
<td>1102</td>
</tr>
<tr>
<td>n-Butane</td>
<td>5</td>
<td>Acetone</td>
<td>1051</td>
</tr>
<tr>
<td>cycloPentane</td>
<td>104</td>
<td>2-Butanone (MEK)</td>
<td>1052</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>8</td>
<td>Benzene</td>
<td>501</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>7</td>
<td>Toluene</td>
<td>502</td>
</tr>
<tr>
<td>cycloHexane</td>
<td>137</td>
<td>m-Xylene</td>
<td>506</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>11</td>
<td>p-Xylene</td>
<td>507</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>17</td>
<td>Phenol</td>
<td>1181</td>
</tr>
<tr>
<td>n-Octane</td>
<td>27</td>
<td>MethylCycloHexane</td>
<td>138</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>46</td>
<td>Nitrogen</td>
<td>905</td>
</tr>
<tr>
<td>n-Decane</td>
<td>56</td>
<td>Carbon dioxide</td>
<td>909</td>
</tr>
</tbody>
</table>

10.1.2 Structure

The structure is a string representation of the components chemical structure (as far is possible) which enables ChemSep to search components by chemical structure parts. It also stores the atoms that make up the molecule. This can be used to generate the overall formula (which is also displayed) or to in estimation methods that use atom contributions.

10.1.3 Family

This indicates the family to which the molecule belongs (alkanes, alkenes, acids, etc.). The family type can be used in the model selection for diffusivities and other properties.

10.1.4 Critical properties and triple/melting/boiling points

The critical properties consist of the critical temperature (K), pressure (Pa), volume ($m^3$), and the critical compressibility factor. These properties are used in many models, most importantly thermodynamic models such as equations of state or corresponding states models.
The normal boiling point (K), melting point (K, Pa) are used in temperature checks during the simulation. ChemSep does not (yet) perform any stability calculations with solids and therefore has only simple warnings regarding this matter. The normal boiling point is used in various thermodynamic models (for example for the vapor pressure).

10.1.5 Molecular parameters

These consist of properties such as the molecular weight (kg/kmol) and liquid molar volume (m³/kmol, at the normal boiling point). The molecular weight is required for all the mass calculations as well as many other things such as concentrations. The acentric factor (also known as \(\omega\)) is most noticeably used in the equation of states and corresponding states methods. Solubility parameter is used in the Regular activity coefficient model. The Van der Waals volume (m³/kmol) and area (m²/kmol) are used for estimating UNIQUAC R and Q properties (used to calculate surface and volume fractions).

10.1.6 Heats/energies/entropies

Here we define the IG heat and Gibbs energy of formation (J/kmol) that can be used in the calculation of chemical equilibria. Entropy calculations require the IG absolute entropy (J/kmol). The heats of fusion melting point and of vaporization normal boiling point (J/kmol) can be used in thermodynamic models and calculating enthalpies (the difference in enthalpy between vapor and liquid is given by the enthalpy of vaporization for example). The standard net heat of combustion (J/kmol) can be used for?

10.1.7 Temperature correlations

Various properties are very dependent on the absolute temperature. The DIPPR library has an extensive set of these properties that we also included in the component data: solid density (kg/m³), liquid density (kg/m³), vapour pressure (Pa), heat of vaporisation (J/kmol), solid heat capacity (J/kmol/K), liquid heat capacity (J/kmol/K), ideal gas heat capacity (J/kmol/K), second virial coefficient (m³/kmol), liquid viscosity (Pa.s), vapour viscosity (Pa.s), liquid thermal conductivity (W/m/K), vapour thermal conductivity (W/m/K), and surface tension (N/m). We added several methods that are from the book ”Properties of Gases and Liquids” by Reid, Prausnitz and Sherwood (3rd Ed.) and Reid, Prausnitz and Poling (4th Ed.): the ideal gas heat capacity (J/kmol/K), heat of formation (J/kmol), Antoine vapor pressure (Pa), and the liquid viscosity (Pa.s).
The type of temperature correlation is determined by an equation number (see the description of the property models). The minimum and maximum temperature (K) describe the working range of the correlation. Five parameters (A through E) are available. Their units will depend on the correlation type.

The most important temperature correlations are the ideal gas heat capacities. Either one of the two heat capacity correlations must be known in order to calculate any enthalpies in ChemSep.

10.1.8 Miscellaneous parameters

The V star property is used in liquid volume calculations. The Lennard Jones diameter and energy can be used in vapor viscosity and diffusivity calculations. The Rackett parameter is used in the estimation of liquid volumes. It can be used to calculate the volume correction for the SRK EOS for example. The Fuller-Schettler SigmaV is used in the Fuller et al. method for estimating vapor diffusivities. The surface tension at the normal boiling point as well as the Parachor can be used in surface tension calculations. The specific gravity is used in the regular model and is estimating properties for petroleum pseudo components. The Chung association parameter is used for liquid diffusivity estimation.

10.1.9 Thermodynamic model parameters

There are properties that function as parameters for thermodynamic models. To make these real model parameters for the models in question, they are defined separately. These are the acentric factor for the SRK cubic equation of state and the Chao-Seader method, the molar volume for the Wilson activity coefficient model and the Chao-Seader method, and the solubility parameter for the Chao-Seader method. Other component thermodynamic parameters are the R, Q, and Q’ constants for the UNIQUAC activity coefficient model and the k_1, k_2, and k_3 parameters for the PRSV equation of state.

10.1.10 Group contribution methods

ChemSep supports the UNIFAC and ASOG group contribution methods for calculating activity coefficients in vapor-liquid equilibria. The UNIFAC is also available for liquid-liquid equilibria calculations. Three other group contribution methods are to be included in the ChemSep program: GC EOS (for VLE), IDIFAC (for diffusivities), and the modified UNIFAC. These are currently not used.
10.2 Making a new library

To start a new library select the new option from the file menu, and enter the name of the new library and a description for the library when prompted for an "info string". The library will contain no components, and you will have to use the Edit menu to add new or import components.

10.3 Editing a library

The edit menu allows you to change the library label, edit component data, delete / move / import / export / update components, check component data presence, estimate component data, and define Pseudo components (from a file with normal boiling points and specific gravities).

10.3.1 Edit/View Library Label

The label serves as a description of the library.

10.3.2 Change/Browse Component

This option will let you select a component of which you want to edit or peruse the property data. After entry ChemLib will prompt you whether you want to write the information to the library. Be careful! Acknowledging to write the information immediately updates the library and there is no way to recover the previous data if you made a mistake.

10.3.3 Deleting Components

To delete components from a library, select the component you want to delete. You can only delete one component at a time.

10.3.4 Moving Components

To move components from the current library to somewhere else, use the Move option in the Edit menu. Select the component to move and a library where to move the component to. You can only select one component to move at a time.
10.3.5 Importing/New Components

You can import or add a new component into the loaded library, either by entering a new component from the keyboard or by importing it from a text file with the component data, from another library, or from a DIPPR data file. The latter are text files with component data which follow the DIPPR format. It is also possible to only import one type of property for multiple components from a text file.

10.3.6 Exporting Components

Similarly to importing you can export component data of components residing in the loaded library to the screen, to a text file, or to another library. It is also possible to export one property for a selection of components to a text file.

10.3.7 Updating Components

Instead of importing you can update the component data. This means that only undefined (empty) data fields will get imported. Component data from multiple sources can be gathered this way.

10.3.8 Checking Components

Once you have collected component data you might want to check it for missing data. Use the check option to write a report to a text file of a selection of components in the current library. Different levels of checking are allowed: essential data, preferred data, optional data, reactions data, or all data.

10.3.9 Estimating Components

If you want to estimate essential data that is missing you can do so with various estimation methods for a selection of components. First select the estimation methods, than the components for which to estimate the data. You find a description of the estimation below, under estimating properties for a new component.
10.3.10 Making Pseudo Components

Pseudo components can be generated when you have a list of the normal boiling temperature (1 atm) and specific gravity of the mixture for which you want to make a pseudo component definition. The method assumes you are trying to estimate properties of a petroleum derivative.

10.3.11 Estimating Properties for a New Component

When you import a new component from the keyboard, the component will be completely undefined. Select the last option, estimate properties, to estimate component property data. The Joback (1984) and Constantinou & Gani (1994) methods are using the UNIFAC groups to estimate the properties. The Riazi Daubert (1980), Twu (1986), and Soave (1998) methods use the normal boiling point temperature and the specific gravity to estimate component properties. Only data that is not yet defined will be calculated, and the data that is already present can be used in the estimation of other properties.

10.3.12 UNIFAC methods

The Constantinou & Gani (GC) group method uses the UNIFAC groups and can be used directly. However, the groups in the Joback method differ from the UNIFAC groups and a translation table was set up from UNIFAC to Joback groups (this table is not complete and could potentially create errors). The properties that are estimated are the critical temperature, pressure, and volume (hence, also the compressibility), the normal boiling point, and the melting point. The (RPP) gas heat capacity, heat of formation, and the gibbs energy of formation can also be estimated using either the Joback group method, or a group method described in Perry’s (6th Ed.) or by Harrison and Seaton (1988) which only predicts the heat capacity.

The Chicks method is used to approximate the heat of fusion at the melting temperature. This is a group method that requires some knowledge of the rings and the number of functional groups that cannot be easily extracted from the UNIFAC groups. Therefore, the method has been partially implemented. As the method directly multiplies the melting temperature with the entropy of fusion, a large error can be expected if the melting temperature is estimated. Thus, errors for the estimated heat of fusion can easily be large. An average error of 25% was calculated for four test molecules.

If we are using the Joback method the acentric factor is calculated using the Lee-Kesler equation, otherwise it is estimated with the GC method. The UNIQUAC R and Q parame-
ters are determined by the UNIFAC groups, and the van der Waals properties are computed directly from \( R \) and \( Q \). The molecular weight is calculated by parsing the atoms in the UNIFAC groups (for some groups this will **NOT** work) and so is the Fuller et al diffusion sigma volume and the components formula (which is used as the name). The heat of vaporization at \( \text{Teb} \) is computed from Vetere’s correlation. The Rackett parameter is computed with:

\[
Z_{\text{Rb}} = 0.29056 - 0.08775\omega
\]  

(10.1)

and the Parachor with the method by Zuo *et al.* The heat of combustion is estimated with

The methods that use the normal boiling point temperature and the specific gravity methods are typically applied for estimating properties of petroleum distillate cuts. The Riazi Daubert (1980) is the most comprehensive. It estimates the molecular weight, critical pressure and volume, liquid volume, refractive index, latent heat, and specific heat. From these the acentric factors is calculated with the Lee Kesler method. From correlations from

\[
S(298) = \sum_i S_i + \Delta S_f(298)
\]  

(10.2)

where the entropy of formation is computed from the Heat and Gibbs free energy of formation:

\[
\Delta S_f(298) = \Delta H_f(298) - \Delta_f(298)/over298
\]  

(10.3)

and the \( S_i \) is the absolute entropy of the element \( i \). To compute this sum the following expression is used when the number of atoms in the molecule are known:

\[
S_i = 10^5 \left( 0.0574 N_c + 1.30571 N_h/2 + 2.02682 N_f/2 + 2.22972 N_{cl}/2 + 1.5221 N_{br}/2 + 1.1614 N_i/2 + 0.32054 N_{other} \right)
\]  

(10.4)

Here \( N_c \) is the number of carbon atoms, \( N_h \) the number of hydrogen atoms, etc. (the state of the elements is gas, except for C, S, and \( I_2 \) which are crystals, and \( Br_2 \) which is a liquid at 298 K and 1 atm. Source Perry’s 7th Ed.).

### 10.3.13 Tb and SG methods

The methods that use the normal boiling point temperature and the specific gravity methods are typically applied for estimating properties of petroleum distillate cuts. The Riazi Daubert (1980) is the most comprehensive. It estimates the molecular weight, critical pressure and volume, liquid volume, refractive index, latent heat, and specific heat. From these the acentric factors is calculated with the Lee Kesler method. From correlations from
Speight (1991) and Soave (1998) the atomic composition is estimated, as well as the heat of combustion, the Fuller diffusion volume, and the Antoine vapor pressure parameters. The Twu (1986) method predicts the molecular weight, critical pressure, temperature and volume. It uses the Lee-Kesler method to estimate the acentric factor. The Soave (1998) method predicts the critical pressure and temperature. It uses the Lee-Kesler method to estimate the acentric factor.

10.4 Other ChemLib Files

Miscellaneous ChemLib files include:

- CHEMLIB.UDF: Units Definition File
- CHEMLIB.HLP: HeLP file
- CHEMLIB.CNF: the default CoNFiguration file
- CHEMLIB.SCR: the additional introduction SCReen(s)

10.5 References


Index

This chapter will contain an index of all subjects, keywords, models etc.