ON SOME REDUCED ORDER MODELS FOR PACKED SEPARATION PROCESSES

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ABSTRACT

The use of packed-bed separation columns as a liquid-gas contact system in absorption and distillation has steadily increased in the chemical and process industries and with it the need for tools for their adequate design and control. The mathematical models for packed separation columns are known for their large dimensionality. This can pose a problem when one considers the design and/or optimisation of systems involving more than one column or a single large column. The use of reduced-order models came as an answer to this problem. Reduced-order models presented to date do not rigorously solve the mass transfer subproblem.

Four generalised steady-state reduced-order models for separation processes in packed columns are developed and compared in this work. The models are based on the two film theory of mass transfer and the more rigorous of them have as a starting point one of the so called rate based methods. The mass and energy transfer rates across the vapour liquid interface are evaluated by means of different approximate solutions of the Maxwell-Stefan equations for steady-state, unidirectional mass transfer. The differential equations of the models are converted into algebraic equations through the application of the orthogonal collocation procedure on the spatial variable. The resulting system of algebraic equations is subsequently solved using a modification of the Powell hybrid method. Three case studies dealing with distillation columns are presented but the models are easily modified to work with other separation processes (e.g., absorption).

The results of the simulations indicated a clear advantage when using more rigorous methods for the computation of the interphase mass transfer rates. Their inclusion in the reduced-order models improved the convergence characteristics of the solution with respect to the number of collocation points and also increased the robustness of the models in converging towards the solution. These improvements were obtained without increasing significantly the time spent in the simulations when compared with a model using an effective diffusivity approach in the evaluation of the mass transfer rates.
Gabriel

Beto Guedes e Ronaldo Bastos

É só de ninar
É de desejar que a luz do nosso amor
Materia prima desta canção
Fique a brilhar

É pra você
É pra todo mundo que quer trazer assim
À paz no coração
Meu pequeno amor

É de você me lembrar
Toda vez que a vida mandar olhar pro céu
Estrela da manhã
Meu pequeno grande amor

Que é você Gabriel
Prá poder ser livre como a gente quis
Quero te ver feliz

Ao que está por vir !!!
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Chapter 1 - Introduction

1- INTRODUCTION

In the beginning, distillation was just a rudimentary technique for the production of liquors through the concentration of the alcoholic content of beverages.

With the passage of the years, distillation developed tremendously to become the most used and important unit operation of the chemical and process industries.

Distillation was performed traditionally in tray columns and only in recent years an increase in the use of packed distillation columns has been seen. For this historical reason almost all the design and/or simulation of packed distillation columns are made using techniques developed for tray columns.

Considering the increasing complexity of chemical processes, together with the need to incorporate energy integration in the design, there is clearly an opportunity for the introduction of optimisation procedures. Equation-based optimisation requires the use of process models that accurately describe the phenomena taking place in the equipment. However, the optimisation of systems involving more than one column or a single large column can be extremely time consuming due to the complexity and large dimensionality of the mathematical model to be solved. The same concern with the size of the models exists in control system synthesis studies where repeated simulations are necessary.

This need for more efficient process models requiring less solution effort gave rise to the development of several procedures for the reduction of the order of the models. It is clear that, on one hand, the reduced-order models must retain certain properties from the rigorous models (e.g., must retain the necessary gradient information of the rigorous model to ensure convergence to the optimum of the rigorous model) but, on the other hand, the dimensionality of the equations involved and the computation speed must not be compromised.
Orthogonal collocation is one of the best known methods for the numerical solution of differential equations in Chemical Engineering models. In the last ten years or so, there has been a great interest on the development of reduced-order models for distillation columns based on the orthogonal collocation procedure. Apart from a small number of exceptions, this effort has been concentrated in modeling tray columns.

The aim of this work is to develop steady-state reduced-order models for packed separation processes in general, and for distillation in particular. These reduced-order models are intended to incorporate in their core a more rigorous approach (when compared with the current standards for reduced-order models) in the evaluation of the interphase mass transfer rates.

As the starting point, in chapter 2, a review of the so called rigorous methods for multistaged separation columns will be presented. Some emphasis will be given to the rate based methods as they are intended to be the basis of the reduced-order models to be developed. This will be followed, in chapter 3, by an analysis of the reduced-order models based on the orthogonal collocation method. As already mentioned, most of the work reported in the open literature deals with tray columns. Nevertheless, there are many lessons to be learned from these experiences.

The necessary tools to rigorously analyse multicomponent mass transfer are discussed in chapter 4. These rigorous computations will need to be backed by the evaluation of several properties of the system. This will be dealt with in chapter 5.

Chapters 6, 7, and 8 are devoted to a comprehensive description of the reduced-order models developed in this work while chapters 9, 10, and 11 will present the results of three case studies.

Finally, in chapter 12, some conclusions on the performance of the reduced-order models are presented together with some topics that deserve further research.
2- RIGOROUS METHODS FOR THE SIMULATION OF MULTISTAGED SEPARATIONS

2.1- INTRODUCTION
One of the basic aims of this work is to develop some models for the simulation of packed separation processes. As Krishnamurthy and Taylor (1985c) pointed out, there are basically two different approaches for modelling packed columns. One of these approaches is to divide the continuous contact device into several sections, where each of the sections is considered as if it were a stage in a stagewise contactor. Therefore, as our final aim is to develop some reduced-order models for the simulation of packed columns, some of the most important rigorous methods for the simulation of multistaged separation processes will be presented in this chapter.

In section 2.2 some methods based on the equilibrium-stage concept are presented while the rate based methods (also known as nonequilibrium stage models) are presented in section 2.3. Some information on where to find guidelines on choosing the appropriate method for a specific application is presented in section 2.4. Finally, in section 2.5, some of the key concepts for the simulation of packed separation columns are discussed.

2.2- MODELS BASED ON THE EQUILIBRIUM-STAGE CONCEPT

2.2.1- The equilibrium-stage
Most of the simulation packages available nowadays for the simulation of multicomponent multistage separations are based on the equilibrium stage concept.

A scheme of a typical equilibrium-stage is presented in Figure 2.1 where the index \( j \) refers to the stage number and \( i \) to the component. A separator consists of a number of such stages arranged in a countercurrent cascade. The stages are numbered down from the top of the column. There is no limitation on the number of components, but it is assumed that no chemical reaction occurs. All
phases leaving the stage are considered to be at thermal and mechanical equilibrium.

![Diagram of an equilibrium-stage](image)

**Figure 2.1. Sketch of the equilibrium-stage**

### 2.2.2- Basic equations for the equilibrium-stage

The equations used to describe the steady state operation of a distillation column are often referred to as the MESH equations [after the work of Wang and Henke (1966)]. The MESH acronym stands for:

- **Material balance for each component** (*nc* equations per stage)

\[
M_{i,j} = L_{j-1} x_{i,-1} + V_{j+1} y_{i,j+1} + F_j z_{i,j} - \left( L_j + S_{i,j} \right) x_{i,j} - \left( V_j + S_{i,j} \right) y_{i,j} = 0 \quad (2.1)
\]

- **Equilibrium relation for each component** (*nc* equations per stage)

\[
E_{i,j} = y_{i,j} - K_{i,j} x_{i,j} = 0 \quad (2.2)
\]

The equilibrium constant, \( K_{i,j} \), is usually a complex function of the general form

\[
K_{i,j} = K_{i,j} \left( T_j, P_j, x_{i,j}, y_{i,j} \right) \quad (2.3)
\]
Chapter 2 - Rigorous Methods for the Simulation of Multistaged Separations

- Mole fraction summations (one equation per stage)

\[ (S_y)_j = \sum_{i=1}^{nc} y_{ij} - 1.0 = 0 \]  \hspace{1cm} (2.4)

\[ (S_x)_j = \sum_{i=1}^{nc} x_{ij} - 1.0 = 0 \]  \hspace{1cm} (2.5)

- Heat or enthalpy or energy balance (one equation per stage)

\[ H_{ij} = L_{j-1} H_{j-1}^L + V_{j+1} H_{j+1}^V + F_j H_j^F - (L_j + S_{L,j}) H_j^L - (V_j + S_{V,j}) H_j^V - Q_j = 0 \]  \hspace{1cm} (2.6)

The enthalpies for each phase are functions of temperature, pressure and composition and the relations have the general form

\[ H_j^l = H_j^l (T_j, P_j, x_{i,j}) \]  \hspace{1cm} (2.7)

\[ H_j^v = H_j^v (T_j, P_j, y_{i,j}) \]  \hspace{1cm} (2.8)

Equation (2.4) or (2.5) can be replaced by a total material balance obtained through the combination of equations (2.4), (2.5) and (2.1) summed over the \( nc \) components and over stages 1 to \( j \) leading to

\[ L_j = V_{j+1} + \sum_{k=1}^{j} (F_k - S_{L,k} - S_{V,k}) - V_1 \]  \hspace{1cm} (2.9)

Sometimes the bubble-point and dew-point equations are used in the solution method to help in the determination of the stage temperature. These equations are generated via the combination of the summation equation and the equilibrium equation, leading to the bubble-point equation

\[ B_j = \sum_{i=1}^{nc} K_{i,j} x_{i,j} - 1 = 0 \]  \hspace{1cm} (2.10)

and the dew-point equation

\[ D_j = \sum_{i=1}^{nc} y_{i,j} K_{i,j} - 1 = 0 \]  \hspace{1cm} (2.11)
A countercurrent cascade of \( N_s \) equilibrium-stages is represented by \( N_s(2n_c+3) \) MESH equations. If all \( F_j, z_{ij}, T_f^i, P_f^i, \) \( P_j, S_{ij}, S_{Lj} \) and \( Q_j \) are specified the system of \( N_s(2n_c+3) \) nonlinear algebraic equations can be solved for the \( N_s(2n_c+3) \) variables \([x_{ij}, y_{ij}, T_j, V_j \text{ and } L_j]\).

\[2.2.3- \text{Classification of the methods of solution}\]

There is in the open literature a wide variety of methods to solve the system of equations presented in the previous section.

Lewis and Matheson (1932) and Thiele and Geddes (1933) are among the first to address the solution of this system of equations in a stage-by-stage, equation-by-equation calculation procedure based on equation tearing. These methods were widely used for hand calculations of simple fractionators with one feed and two products. In the first attempts to program the Thiele-Geddes method in a digital computer the solution procedure was often numerically unstable [Henley and Seader (1981)].

Several improvements in these early methods were presented in the literature and in a classic study, Friday and Smith (1964) analysed a number of tearing techniques for the solution of the MESH equations. They concluded that no single technique is able to handle all types of problems. They also divided the rigorous methods of solution into four basic classes, namely:

- bubble-point methods (BP);
- sum-rates methods (SR);
- the 2N Newton methods;
- the global Newton or simultaneous correction methods (SC).

The continuous development of new techniques led Haas (1992) to add some classes to the previous ones, for example:

- inside-out methods;
- relaxation methods;
- homotopy-continuation methods.
In the following sections a brief description of some of the most important methods of each class will be presented.

2.2.4- Tridiagonal matrix algorithm

The tridiagonal matrix algorithm, introduced by Wang and Henke (1966) for calculating the component and total flowrates, is used in most of the methods presented in this chapter.

The tridiagonal matrix results from a modification of equation (2.1). The vapour mole fractions are eliminated from equation (2.1) using equation (2.2) and the total liquid flowrates are eliminated via substitution of equation (2.9) into equation (2.1). The resulting equation for component \( i \) in stage \( j \) is:

\[
L D_j x_{i,j-1} + U D_{i,j} x_{i,j} + U D_{i,j} x_{i,j+1} = U_{i,j} \tag{2.12}
\]

where

\[
L D_j = V_j + \sum_{k=1}^{j-1} (F_k - S_{L_k} - S_{V_k}) - V_1
\]

\[2 \leq j \leq N_S \tag{2.13}\]

\[
U D_{i,j} = -\left[ V_{j+1} + \sum_{k=1}^{j} (F_k - S_{L_k} - S_{V_k}) - V_1 + S_{L_{j+1}} + (V_j + S_{V_j}) K_{i,j} \right] \tag{2.14}
\]

\[1 \leq j \leq N_S \]

\[
U D_{i,j} = V_{j+1} K_{i,j+1} \tag{2.15}
\]

\[1 \leq j \leq N_S - 1 \]

\[
U_{i,j} = -F_j x_{i,j} \tag{2.16}
\]

\[1 \leq j \leq N_S \]

and, for a typical distillation column, \( x_{i,0} = 0 \), \( V_{N_L+1} = 0 \), \( S_{V_i} = 0 \) and \( S_{L_{V_i}} = 0 \).

Grouping equations (2.12) by component they can be partitioned in \( nc \) tridiagonal matrix equations as follows:
Chapter 2 - Rigorous Methods for the Simulation of Multistaged Separations

It is important to emphasise that $^MD_{ij}$ and $^UD_{ij}$ depend only on the tear variables (the vector of temperatures and the vector of vapour flow rates) provided that the values of $K_{ij}$ are composition independent. If not, compositions from the previous iteration may be used to estimate the values of $K_{ij}$.

The output variables of each equation (2.17) are the liquid mole fractions of component $i$ over the whole column ($N_s$ stages).

There are some solution techniques specially tailored for tridiagonal matrices. In their work Wang and Henke (1966) recommended the usage of an algorithm developed by Thomas [Lapidus (1962)]. Boston and Sullivan (1972) presented a modified Thomas algorithm that is able to handle difficult problems that arise with columns with a great number of stages and with components whose absorption factors vary significantly from top to bottom of the column.

2.2.5- Bubble-point methods

In this class of methods the stage temperatures are calculated by solving the bubble point equation. These methods are generally used for narrow-boiling, nearly ideal systems.

The Wang and Henke (1966) method uses the tridiagonal matrix to calculate the compositions and those are used to calculate the temperatures by solving the bubble-point equation.
To start the iterative procedure one must assume values for the tear variables. Frequently the assumption of constant molar interstage flows is a good starting point. For the initial values of the vector of temperatures it is common practice to assume a linear variation of the temperature with stage location. The top temperature can be estimated from the bubble-point of the assumed liquid distillate product and the bottom temperature from the dew-point of the assumed bottom product. If the values of $K_{ij}$ are composition dependent one also needs to estimate the initial liquid and vapour composition profiles. Alternatively, ideal values of $K_{ij}$ can be used for the first iteration.

The corrected values of the flow rates are computed using equations (2.6) and (2.9). The procedure is considered to be converged when the variations between two consecutive sets of temperatures and between two consecutive sets of flow rates are smaller than a specified tolerance. Frequently successive substitution is used to update the tear variables.

An interesting alternative is to use the tridiagonal method to calculate the compositions but a new direct procedure to evaluate temperatures avoiding the iterative bubble-point temperature determination. This procedure, named the $K_{ij}$-method, is an approximation of the dew or bubble-point equations and it is one of the key features of the theta-method of Holland and co-workers [Holland (1975)]. In the theta-method a convergence promoter, $\theta$, is used to correct the calculated values of the component flow rates obtained from the solution of the tridiagonal matrix before they are used in the estimation of the stage temperatures. The convergence promoter is used to force the overall component balance as well as the total material balance to be satisfied. This step is necessary since the flowrates of each component come from different tridiagonal systems.

### 2.2.6- Sum-rates methods

The key characteristic of sum-rates' methods is that they use the energy balances to calculate the stage temperatures. Those methods can be applied
to distillation but the reboiler and the condenser must be solved as separate unit operations [Fonyo et al. (1983)]. Sum-rates' methods are suited to modelling absorbers and strippers, being able to simulate some extremely wide boiling systems containing noncondensables.

Probably the most commonly used sum-rate method is the one developed by Burningham and Otto (1967). The temperatures are calculated via the solution of the stage energy balances using a Newton-Raphson technique [a comprehensive discussion of the Newton-Raphson method and its variants can be found in Holland (1981)]. Component flow rates are then evaluated using the tridiagonal matrix algorithm. The component flow rates are then added to get the total flow rates, a procedure that gives the name of the method (sum-rates).

2.2.7- 2N Newton methods

Unlike in the bubble-point and sum-rates' methods in the 2N Newton methods the temperatures and total flow rates are calculated in the same step using a Newton-Raphson algorithm. The component flow rates are calculated in a separate step. The name 2N is due to the necessity of writing down two equations per stage, leading to a total of 2N equations (considering N the number of stages).

These methods are a good alternative for systems involving the separation of wide or middle boiling mixtures.

In his formulation Tomich (1970) uses as the first function a combination of the summation equations for the vapour and liquid compositions [equations (2.4) and (2.5)]. The second independent function is the stage energy balance. The total vapour flow rates and the temperatures are chosen as the independent variables.
To start the iterative procedure one should guess initial values for the temperatures and total vapour flow rates. The next step is to evaluate the liquid compositions using the tridiagonal algorithm. A new set of temperatures and total vapour flow rates is then obtained via one single iteration of the Newton-Raphson algorithm. If the norm of the functions is very small and any other specified criteria are also met the final solution was reached. Otherwise the whole procedure is repeated on the basis of the new set of temperatures and total vapour flow rates.

Holland (1981) made a different choice on the functions and variables for the Newton-Raphson iteration. The independent functions are either the dew-point or bubble-point equations [equations (2.10) or (2.11)] and the energy balances. The independent variables are the temperatures and $\Xi_j$ a multiplier defined as follows:

$$
\begin{bmatrix}
\frac{L_j}{V_j} \\
\frac{L_j}{V_j}
\end{bmatrix}_{co} = \Xi_j \begin{bmatrix}
\frac{L_j}{V_j} \\
\frac{L_j}{V_j}
\end{bmatrix}_{ca}
$$

(2.18)

The corrected values of the ratio $L_j/V_j$ are used in the absorption and stripping factors employed in the component balances and in the total material balance.

The calculation sequence to be adopted is similar to that of Tomich (1970).

### 2.2.8- Simultaneous correction methods

The basic characteristic of the simultaneous correction methods is that they attempt to solve all the MESH equations and variables together. Although they are the most powerful in solving problems involving nonideal mixtures they present the weakness of being extremely sensitive to the set of initial values. Frequently there is the need to use another rigorous method to produce a good set of starting values for the simultaneous correction methods.
Chapter 2 - Rigorous Methods for the Simulation of Multistaged Separations

In the Naphtali-Sandholm method [Naphtali and Sandholm (1971)] the chosen independent variables for the Newton-Raphson calculation are the stage temperatures and component liquid and vapour flow rates. The independent variables are grouped by stage and ordered as presented above. The independent functions for a stage are the energy balance, one equilibrium equation for each component and one component balance for each component.

In order to keep the numerical values in the same order of magnitude the independent functions are written in a normalised form.

These equations are grouped by stage and their order of appearance in the vector of functions is first the energy balance, second the component balances and finally the equilibrium equations. This will lead to a total of \(2nc+1\) equations and variables per stage.

All the variables are solved together producing a Jacobian of size \(N_s(2nc+1) \times N_s(2nc+1)\). Due to the chosen grouping and ordering of the equations the Jacobian will be sparse with a block-banded structure (blocks of elements along the main, upper, and lower diagonals).

Starting from an initial set of temperatures and total vapour and liquid flow rates for each stage the initial component liquid and component vapour flow rates are calculated using the tridiagonal matrix algorithm. The results of the previous step are then used to initialise the Newton-Raphson procedure that will iterate until the norm of the independent function residuals is very small and any other criteria specified are satisfied. The total flow rates and the duties are calculated only after the solution is found.

There are in the open literature many other simultaneous correction methods [e.g., Ishii and Otto (1973), Gallun and Holland (1976)] that introduce some kind of improvement on the Naphtali and Sandholm (1971) method.
2.2.9- **Inside-out methods**

Nowadays the inside-out methods are among the most popular methods due to their flexibility and robustness.

In the methods presented in the previous sections every time the MESH variables change there is the need to update the equilibrium constants, $K_{ij}$, and the enthalpies using complex correlations.

The basic idea of the inside-out methods is to employ simple enthalpy and equilibrium constant models together with the MESH equations in a so called inside loop where the MESH variables are calculated (using variations of the methods presented before, e.g., bubble-point, 2N Newton). Then, on the basis of the most recent set of MESH variables, the parameters for the simple enthalpy and equilibrium constant models are updated using the complex enthalpy and equilibrium constant correlations on the outer loop. It is important to stress that the parameters of the simple models are unique for each stage and are the variables of the outer loop.

As a consequence of the simplicity of the enthalpy and equilibrium constant models the inside loop is remarkably stable for a wide range of mixtures.


2.2.10- **Relaxation methods**

Rose *et al.* (1958) presented the first version of a relaxation method. Several improvements were then introduced by, among others, Jelínek *et al.* (1973), Ketchum (1979) and Mori *et al.* (1987).

The steady-state solution of a column is determined in a relaxation method by successive approximations of the unsteady-state distillation equations. Some
realistic condition is used as the starting point to the integration scheme.

In the early methods only the component balances were written in a time-dependent form as follows:

\[
\left( V_{j+1, i}, y_{i,j+1} + L_{j-1, i,j-1} - V_{j, i,j} - L_{i,j} x_{i,j} \right) M_j \frac{dx_{i,j}}{dt} = (2.19)
\]

where the vapour holdup was considered negligible and the liquid holdup assumed to be constant. The composition after a time interval \( \Delta t \) is calculated using Euler's method:

\[
x_{i,j}\bigg|_{t+\Delta t} = x_{i,j}\bigg|_t + \Delta t \frac{dx_{i,j}}{dt}\bigg|_t (2.20)
\]

In the relaxation equations the \( K \)-values and the total flowrates are considered constants from one time step to the next. Once a new set of compositions is obtained, the equilibrium constants are updated and the remaining MESH equations are solved by one of the previous conventional solution methods.

Ketchum (1979) presented a review of relaxation methods and discussed three of their main weaknesses:

- since the temperatures and total flow rates are calculated separately from the compositions the temperature correction can be unstable or very slow;
- in the calculation there is no estimation on the variation of temperature with time;
- in order to prevent instability the time step is kept small and this will cause the method to move slowly, especially close to the steady-state condition.

Trying to eliminate such problems Ketchum (1979) transforms the global Newton method of Naphtali and Sandholm (1971) into a relaxation method. Now the variation of the temperature with time is expressed by

\[
T_j\bigg|_{t+\Delta t} = T_j\bigg|_t + \Delta t \frac{dT_j}{dt}\bigg|_t (2.21)
\]
and one must include in the independent functions the transient version of the energy balance of each stage, written as

\[
\frac{1}{\bar{C}^L_{m}} \sum_{j=1}^{\infty} I_{j} = \frac{1}{\bar{C}^L_{m}} \sum_{j=1}^{\infty} I_{j-1} - \frac{dT_j}{dt}
\]  

Depending on the size of the time step the method behaves as a relaxation or as a global Newton method. When the \( \Delta t \) is small the changes in the independent variables are small and the method behaves as a damped Newton-Raphson method that moves slowly and monotonically towards the solution. On the other hand if \( \Delta t \) is large the method performs as a Newton-Raphson method.

Therefore Ketchum's relaxation method is fast and stable because one can start with a small time step and proceed with it until the changes in the temperature and liquid compositions become small. The time step is then increased, switching to the global Newton-Raphson part of the algorithm. In other words the relaxation method is used to produce very good starting values for the global Newton method.

### 2.2.11- Homotopy-continuation methods

The homotopy or continuation methods start from a known solution of the column and then follow a path towards the desired solution. The known solution can be at different conditions or employing simpler correlations for the evaluation of equilibrium constants and enthalpy making the solution easy to be obtained.

The homotopy function is a blend of two functions

\[
h(x, t_h) = t_h f(x) + (1-t_h)g(x)
\]  

where \( g(x) \) is the known or simpler solution and \( f(x) \) is the difficult solution of the column. The homotopy parameter \( t_h \) will vary from zero to one making the
solution travel from the known solution to the difficult one. Any new value of $t_h$ will produce a different set of independent variables $x$. The final solution is found when $f(x) = 0$ which causes at $t_h = 1 \rightarrow h(x, t_h) = 0$.

The homotopy methods can be divided into mathematical homotopies and physical or parametric homotopies. The physical homotopies have a basis in the MESH equations and, as pointed out by Taylor et al. (1987), they perform better than the mathematical homotopies.

Vickery and Taylor (1986) developed a thermodynamic homotopy on which ideal equilibrium constants and ideal enthalpies were used at the beginning of the procedure and then were slowly switched to the rigorous equilibrium constants and rigorous enthalpies by changing the value of the homotopy parameter.

The steps of their homotopy method are as follows:

1. set up initial values (temperatures and total vapour and liquid flow rates for every stage) and find out the known (easy) solution;
2. the homotopy parameter is set to zero. The solution of step 1 is the initial value to $x$;
3. solve $h(x, t_h) = 0$ using a global Newton method;
4. if $t_h < 1$ the current values of $(dx/dt_h)$ are calculated from:
   \[
   \left[ \frac{\partial h}{\partial x} \right] \left( \frac{dx}{dt_h} \right) + \left( \frac{\partial h}{\partial t_h} \right) = 0
   \]  
   (2.24)
5. use Euler's rule to calculate the new value of $x$ and return to step 3
   \[
   x|_{k+1} = x|_k + \Delta t_h \left( \frac{dx}{dt_h} \right)_k
   \]  
   (2.25)

Taylor et al. (1987) presented a physical homotopy based on a pseudo-Murphree efficiency. Such pseudo efficiency is varied from, for example, 0.1, a situation where very little separation is achieved, to a maximum of one at the final solution.
2.3- RATE-BASED METHODS

The basic idea behind the rate-based methods (also known as 'nonequilibrium methods') is to apply an approach based on transport phenomena in order to evaluate the mass transfer rates taking place in real trays of the column. In that sense they throw away concepts like the equilibrium-stage and efficiencies of the trays, columns and packings.

The most successful of the nonequilibrium methods is the one developed by Krishnamurthy and Taylor (1985a, 1985b). This model allows one to simulate not only tray columns but also packed ones in the steady state. A sketch of a nonequilibrium stage is presented in Figure 2.2. A packed tower or a multitray column is modelled by a sequence of such stages. The stage is assumed to be at mechanical equilibrium which means the pressure is considered constant on the stage.

![Figure 2.2. Sketch of the nonequilibrium stage](image)

In the same way as with the equilibrium-stage models the starting point is the development of material and energy balances. There is a big difference between the methods because here the balances are split into two parts, one for each phase.
The component mass balance for the vapour phase is
\[ M_{ij}^\gamma = (1 + r_j^\gamma) v_{i,j} - v_{i,j+1} - f_{i,j}^\gamma + \mathcal{M}_{ij}^\gamma = 0 \] (2.26)
where
\[ r_j^\gamma = S_{ij} / V_j \] (2.27)
and for the liquid phase
\[ M_{ij}^L = (1 + r_j^L) \ell_{i,j} - \ell_{i,j-1} - f_{i,j}^L - \mathcal{N}_{ij}^L = 0 \] (2.28)
where
\[ r_j^L = S_{ij} / L_j \] (2.29)
\[ \mathcal{M}_{ij}^L \text{ and } \mathcal{N}_{ij}^\gamma, \] the net loss or gain of component \( i \) due to interphase transport can be formally written as:
\[ \mathcal{M}_{ij}^L = \int N_{i,j}^L \, da_j \text{ and } \mathcal{N}_{ij}^\gamma = \int N_{i,j}^\gamma \, da_j \] (2.30)
The energy balance for the vapour phase is given by:
\[ E_j^\gamma = (1 + r_j^\gamma) v_j h_j^\gamma - v_{j+1} h_{j+1}^\gamma + Q_j^\gamma - F_j^\gamma h_{j}^{\gamma f} + \mathcal{E}_j^\gamma = 0 \] (2.31)
and for the liquid phase
\[ E_j^L = (1 + r_j^L) \ell_j h_j^L - \ell_{j-1} h_{j-1}^L + Q_j^L - F_j^L h_{j}^{L f} - \mathcal{E}_j^L = 0 \] (2.32)
The net loss or gain of energy due to interphase transport, \( \mathcal{E}_{ij}^\gamma \) and \( \mathcal{E}_{ij}^\gamma \), can be expressed as:
\[ \mathcal{E}_j^\gamma = \int E_j^\gamma \, da_j \text{ and } \mathcal{E}_j^L = \int E_j^L \, da_j \] (2.33)
There is also the need to write down mass and energy balances for the interface. They will be written as:
For the interface model Krishnamurthy and Taylor (1985a) considered a surface offering no resistance to transport and where equilibrium prevails. A scheme of the interface model is presented in Figure 2.3.

![Figure 2.3. Composition and temperature profiles in the region of the interface.](image)

For such a model one can write the following equations:

\[
Q_{i,j}^I = K_{i,j}x_{i,j}^I - y_{i,j}^I = 0 \quad (2.36)
\]

\[
S_{j}^V = \sum_{i=1}^{nc} y_{i,j}^V - 1 = 0 \quad (2.37)
\]

\[
S_{j}^L = \sum_{i=1}^{nc} x_{i,j}^L - 1 = 0 \quad (2.38)
\]

\[
K_{i,j} = K_{i,j}(x_{i,j}^I, y_{i,j}^V, T_{j}^V, P_{j}) \quad (2.39)
\]

In order to complete the model represented by equations (2.26) to (2.39) one needs to specify how the interphase transport rates \( N_{i,j}^V \), \( N_{i,j}^L \), \( S_{j}^V \), and \( S_{j}^L \) will be evaluated.
A rigorous multicomponent mass transfer analysis [see section 4.6 for some alternatives] will lead to rate equations like:

\[ N_i^V = \sum_{k=1}^{nc-1} k_{i,k}^V (y_k^V - y_k^V) + y_i^V N_i^V \tag{2.40} \]
\[ i = 1,2,\ldots, nc-1 \]

\[ N_i^L = \sum_{k=1}^{nc-1} k_{i,k}^L (x_k^L - x_k^L) + x_i^L N_i^L \tag{2.41} \]
\[ i = 1,2,\ldots, nc-1 \]

Since one can only write down \( nc-1 \) equations (2.40) and (2.41) the flux of component \( nc \) will be calculated from the \( nc-1 \) fluxes and the energy transfer rate equations presented below.

\[ E_i^V = q_i^V + \sum_{i=1}^{nc} N_i^V \bar{H}_i^V \tag{2.42} \]

\[ E_i^L = q_i^L + \sum_{i=1}^{nc} N_i^L \bar{H}_i^L \tag{2.43} \]

According to equations (2.30) and (2.33), to calculate the total mass and energy transfer rates, it will be necessary to perform the indicated integrations over some model path.

The authors considered that the interface state is the same throughout the dispersion on a specific stage and that the mass transfer coefficients could be considered constant on any stage. Imposing a particular shape to the bulk phase composition profiles the integrated total transport rates were found to be equal to the average fluxes multiplied by the total interfacial area.

\[ \mathcal{N}_{i,j}^V = N_{i,j}^V a_j \equiv \mathcal{N}_{i,j}^V (k_{i,k}^V a_j, y_k^V, \bar{y}_k^V, T_j^V, T_j, \bar{y}_k^V, \mathcal{N}_{k,j}^V, k = 1,2,\ldots, nc) \tag{2.44} \]

\[ \mathcal{N}_{i,j}^L = N_{i,j}^L a_j \equiv \mathcal{N}_{i,j}^L (k_{i,k}^L a_j, x_k^L, \bar{x}_k^L, T_j^L, T_j, \bar{x}_k^L, \mathcal{N}_{k,j}^L, k = 1,2,\ldots, nc) \tag{2.45} \]

\[ \mathcal{E}_j^V = E_j^V a_j \equiv \mathcal{E}_j^V (h_j^V a_j, T_j^V, T_j, \bar{y}_k^V, \mathcal{N}_{k,j}^V) \tag{2.46} \]

\[ \mathcal{E}_j^L = E_j^L a_j \equiv \mathcal{E}_j^L (h_j^L a_j, T_j^L, T_j, \bar{x}_k^L, \mathcal{N}_{k,j}^L) \tag{2.47} \]
In those last equations the mole fractions $\bar{x}_{i,j}$ and $\bar{y}_{i,j}$ and temperatures $\bar{T}_j$ and $\bar{T}'_j$ represent the integrated average bulk phase conditions. Further details concerning these averages are discussed later in this section.

Considering equation (2.34) one can see that strictly speaking there is only one set of $nc$ independent transfer rates. Thus, combining equations (2.34), (2.44) and (2.45) one will get:

$$R_{i,j}^y = \mathcal{N}_{i,j}^- \left( k_{x,y,j} a_{j}, y_{y,j}, \bar{y}_{y,j}, \bar{T}_{j}, \bar{T}'_{j}, T_{j}, T'_{j}, \mathcal{N}_{j,k}, k = 1,2,\cdots, nc \right) = 0 \quad (2.48)$$

$$R_{i,j}^L = \mathcal{N}_{i,j}^- \left( k_{x,L,j} a_{j}, x_{x,j}, \bar{x}_{x,j}, \bar{T}_{j}, \bar{T}'_{j}, T_{j}, T'_{j}, \mathcal{N}_{j,k}, k = 1,2,\cdots, nc \right) = 0 \quad (2.49)$$

Combining equations (2.35), (2.46) and (2.47) one arrives at the equation:

$$E_{j}^L = \mathcal{O}_{j}^L \left( h_{x,y,j}, \bar{y}_{y,j}, \bar{T}_{j}, \bar{T}'_{j}, \mathcal{N}_{j,k} \right) - \mathcal{O}_{j}^L \left( h_{x,L,j}, \bar{T}_{j}, \bar{T}'_{j}, \mathcal{N}_{j,k} \right) = 0 \quad (2.50)$$

This completes the development of the model. Once the states of all feed streams, the flow rates of all side streams, heat loads, and pressure on the stage are fixed there will be a set of $5nc+1$ equations in $5nc+1$ independent variables to be solved per stage.

The $5nc+1$ variables are ordered into the vector $(x)$ as follows:

$$(x) = \left( v_{t,j}, v_{2,j}, \cdots, v_{nc,j}, T_{j}, T'_{j}, t_{1,j}, t_{2,j}, \cdots, t_{nc,j}, \mathcal{N}_{1,j}, \mathcal{N}_{2,j}, \cdots, \mathcal{N}_{nc,j}, y_{t,j}, y_{2,j}, \cdots, y_{nc-1,j}, T'_{j}, x_{1,j}, x_{2,j}, \cdots, x_{nc-1,j} \right) \quad (2.51)$$

and the corresponding equations are ordered into the vector $(f)$ represented below:

$$(f) = \left( M_{t,j}^V, M_{2,j}^V, \cdots, M_{nc,j}^V, E_{j}^V, E_{j}^L, M_{t,j}^L, M_{2,j}^L, \cdots, M_{nc,j}^L, R_{t,j}^V \right)$$

$$R_{2,j}^L, \cdots, R_{nc-1,j}^L, E_{j}^L, Q_{t,j}^L, Q_{2,j}^L, \cdots, Q_{nc,j}^L, R_{t,j}^L, R_{2,j}^L, \cdots, R_{nc-1,j}^L \right) \quad (2.52)$$

The system of equations $(f)$ is referred as the MERQ equations (Material
balances, Energy balances, Rate equations and Equilibrium equation). To model a column with $N_r$ trays or sections of packing $N_r(5nc+1)$ equations are involved. These equations are arranged to have a block-banded form. To solve the system of algebraic equations (2.52) Krishnamurthy and Taylor (1985a, 1985b) used Newton’s method and the hybrid method of Lucia and co-workers [Lucia and Macchietto (1983), Lucia and Westman (1983)].

This nonequilibrium model was used by Krishnamurthy and Taylor (1985b) to simulate some vapour phase-controlled distillation experiments conducted by several authors in wetted-wall and in bubble cap columns. All the columns simulated were operating at total reflux.

To calculate the mass and energy transfer rates they used the method presented by Krishna and Standart (1979) that is based on an exact solution of the Maxwell-Stefan equations.

In equations (2.44) to (2.47) some average mole fractions were introduced. Krishnamurthy and Taylor (1985b) had assumed a linear variation in the vapour mole fraction between the entering and leaving values, leading to:

$$\bar{y}_{i,j} = \frac{1}{2} \left( \frac{y_{i,j}}{V_j} + \frac{y_{i,j+1}}{V_{j+1}} \right)$$

For the liquid phase they considered a well mixed liquid at the exit composition that can be represented by

$$\bar{x}_{i,j}^L = \frac{l_{i,j}}{L_j}$$

They also report the use of some other definitions for the averages but the definitions presented above gave the best agreement between predicted and experimental values.

Krishnamurthy and Taylor (1985c) used the nonequilibrium stage model to
simulate a packed distillation column and a packed absorber column. These columns were in operation at the Zoller Gas plant in Refugio, TX, USA. Several field tests are reported in Bassyoni (1969), McDaniel (1969) and McDaniel et al. (1970). It is noteworthy that despite the fact that the mixtures separated were multicomponent (twelve components in the distillation column and fourteen in the absorber) the utilisation of various mass transfer models led to results that are not significantly different. This can be explained because the distillation column was fractionating a mixture of hydrocarbons and in the absorber nitrogen and carbon dioxide are trace components. When the system under consideration is like one of these (hydrocarbons of a homologous series) the interaction effects are not very important.

The application of the nonequilibrium stage model to the design of distillation and absorber columns is addressed by Krishnamurthy and Taylor (1985d, 1986) and Sivasubramanian et al. (1987). In the first two papers the results of some design problems using the equilibrium model with stage efficiency determined using the AIChE method [as described by King (1980)] and the nonequilibrium model are compared. The two models predicted very different numbers of stages (differences ranging from 53% to 10% for nonideal systems).

Krishnamurthy and Taylor (1985d) pointed out the importance of considering the liquid phase resistance and the diffusional interactions in some distillation designs: "if the driving forces for mass transfer are small (as they are in extractive and azeotropic distillation and high-purity separations, for example), then the liquid phase resistance may assume greater importance".

Powers et al. (1988) present a discussion of some computational methods to solve the equations of the nonequilibrium model. They addressed the utilisation of a homotopy method similar to those presented by Vickery and Taylor (1986) and Vickery et al. (1988) to solve some difficult distillation problems.

They also demonstrate some concern on the reduction of the time spent on the
solution of the nonequilibrium model when compared with the equilibrium stage model (there are $5nc+1$ equations per stage on the nonequilibrium model and $2nc+1$ equations per stage on the equilibrium stage). One of the suggested alternatives is the "stage lumping", where the column is divided in sections, each representing more than one real tray. Every section is then modelled by a set of $5nc+1$ equations and variables. As expected, the accuracy of the predicted compositions decreased as the number of sections employed was decreased. In order to improve the quality of the results obtained using this "lumping" technique the bulk vapour composition must be evaluated using the following expression

$$\bar{y}_{ij}^{v} = \frac{1}{2n} \left[ \frac{v_{ij}}{V_{j}} + \frac{(2n-1)v_{ij,s+1}}{V_{j,s+1}} \right]$$ (2.55)

where $n$ is the number of "lumped" trays.

The application of the nonequilibrium method into industrial-scale distillation and absorption columns is presented by Taylor et al. (1992). Due to the good agreement between experimental and predicted values and, based on their experience with this new methodology, they recommend its use for the following classes of problems:

- packed columns;
- strongly nonideal systems;
- columns with sharp profiles or containing a maximum;
- columns with multiple feeds and/or sidestreams;
- columns with unknown efficiencies.

### 2.4- Selection of the Method to Use

After ensuring that the problem is well defined it is necessary to select which method is more suitable for the system to be analysed and for the output to be produced.

As shown by Haas(1992), depending on the method to be used it may be
necessary to feed more information in order to initialise the solution procedure. It is also necessary to check if the selected method of solution is able to deal with the kind of specifications to be imposed.

Some very useful guidelines on which method to choose are presented by King (1980). Haas (1992) also presents a very good discussion of the subject and a decision diagram to help in the selection (see Figure 2.4).

2.5- MODELS FOR PACKED COLUMNS

Nowadays the application of packed-bed separation columns has increased in the field of distillation. Unfortunately the modelling work of packed-bed separation processes presented in the open literature is much less than that for staged systems.

The packed column is a non-linear distributed parameter system that needs to be significantly simplified (without losing important information) before any kind of analysis can be performed.

Frequently the engineer that deals with the design of a packed column introduces some simplifying assumptions like the Height of a Transfer Unit (HTU) or the Height Equivalent to a Theoretical Plate (HETP) causing a reduction on the accuracy of the results.

Holland and co-workers [Holland (1975), McDaniel (1968, 1969), McDaniel et al. (1970), Bassyoni (1969)] opted to divide the packed column into increments or discrete mass transfer sections. Such increments are then considered as stages in a tray column. With this approach any of the previously presented methods to deal with tray columns can be used to simulate the packed column.

In their technique the temperatures of the vapour and liquid streams leaving a section are considered to be equal; the errors caused by the introduction of this
Figure 2.4. Method decision diagram [Haas (1992)].
approximation are absorbed in the vaporisation efficiencies that are employed to correct the composition of the exit streams from departures to equilibrium.

Unfortunately these vaporisation efficiencies are not easily computed in advance and therefore they used some field tests in order to estimate these parameters that were then used in further simulations.

Another approach to model the packed column is to write differential mass and energy balances for a small element of packing and to solve them by a numerical integration scheme.

Some researchers have been working attempting to solve the differential equations produced when the two-film concept of mass transfer is applied.

Treybal (1969) presented a solution procedure that for the first time also included the mass and heat transfer resistances of the liquid phase. His procedure was only able to deal with simple three component systems, with only one component being transferred.

This methodology was extended by Feintuch and Treybal (1978) to multicomponent systems. For a specified absorption separation one should guess the conditions of one of the exit streams. Based on the guessed exit stream and with a specified number of packing height increments, a complex iterative procedure, with several levels of nested loops, is used. Kelly et al. (1984) employed this methodology to model the absorption of acid gases in methanol. They made some alterations to the solution algorithm to improve the convergence characteristics of the systems they studied.

von Rosenberg and Hadi (1980) replaced the differential equations by finite difference equations that are then solved using a tridiagonal matrix algorithm. The problem with the finite difference technique is the large number of segments needed to approximate the continuous system.
A big deficiency of the methods listed above resides in the fact that they evaluate the interphase transport rates in a simplified way. The calculation of the rates of mass transfer in multicomponent mixtures is complicated by the coupling, or interaction, between individual concentration gradients. Due to these interactions a species may transfer in the direction opposite to that expected, may not diffuse even though a concentration gradient for that species exists, or may diffuse in the absence of any driving force. The major problem with the effective diffusivity approaches is that they do not accurately reflect the character of multicomponent diffusion.

Smith and Taylor (1983) presented a statistical comparison of film models for multicomponent mass transfer. They compared the rates of mass transfer predicted from several approximate solutions of the Maxwell-Stefan equations for a film model of steady-state diffusion with the fluxes predicted by an exact solution. According to them "the simple effective diffusivity methods are woefully inadequate". A more rigorous multicomponent mass transfer analysis [see Chapter 4 for a discussion of multicomponent mass transfer issues] must be incorporated to produce more reliable results.

Karlström et al. (1992) presented a more rigorous model that also includes the momentum transfer balance in order to simulate the dynamics of a packed column. This model still needs to be properly implemented and tested.

2.6- Conclusions

As Seader (1989) properly stressed, the models based on the equilibrium-stage concept have been widely used in the past years. One of the major weaknesses of these models lies in the uncertainties in assigning or predicting values for the efficiencies of the real trays for multicomponent systems.

On the other hand, the rate based approach avoids these uncertainties through a model that is based on sound mass and heat transfer fundamentals. Seader recommends their usage not only for nonideal multicomponent systems but
also for nearly ideal multicomponent systems when good predictions of product distributions are desired for components other than the key components.

The major problem with the nonequilibrium stage models resides in the large dimensionality of the system of equations to be solved. Even though Powers et al. (1988) have already addressed some issues on how to minimise this problem, some more research needs to be done on this front.
3- REDUCED-ORDER MODELS BASED ON THE ORTHOGONAL COLLOCATION METHOD

3.1- INTRODUCTION

It is well known that one of the major difficulties with mathematical models of separation columns is the large dimensionality of the process model.

In recent years there has been an increasing interest in the development of strategies for the reduction of the order of dynamic systems representing separation columns. The ultimate goal is to develop, starting from the original set of equations, a reduced-order model capable of describing, with good accuracy, the dynamic and the steady state behaviour of the "full" model.

Among many other techniques one that seems very attractive and efficient is the utilisation of the method of orthogonal collocation [Villadsen and Michelsen (1978) and Finlayson (1980)] in the order reduction of the model. The discretization of the spatial variable using the orthogonal collocation technique allows one to:

- transform the system of partial differential equations of the dynamic model of the separation column into a system of ordinary differential equations;
- transform the system of ordinary differential equations of the steady state model of the separation column into a system of algebraic equations.

Aiming for the elaboration of a reduced-order model for the simulation of packed separation columns based on the orthogonal collocation technique some of the most important developments on the subject will be presented in this chapter.

Considerably more work has been done on the order reduction of models for tray columns. As some of these ideas could be extended to packed columns, this chapter presents in section 3.2 a review on the methods for tray columns. On the other hand, section 3.3 will be focused on the methods for packed columns.
3.2- Tray Columns

One of the first published model reduction procedures based on the orthogonal collocation technique was presented by Wong and Luus (1980). The main drawback in their approach is that their approximation does not preserve the material balance in the steady state.

Cho and Joseph (1983a, 1983b) presented a model for sections of countercurrent staged separation systems without intermediate feeds or sidestreams.

The starting point of their procedure is a rigorous tray-by-tray model as described below and based on the following basic assumptions:

- the liquid leaving the tray is well mixed;
- the vapour holdup is negligible compared with the liquid holdup;
- there is a definite relationship between the liquid and the vapour composition leaving a tray;
- vapour and liquid leaving a tray are in thermal equilibrium.

A scheme of the column with the definition of some of the variables involved is presented in Figure 3.1. It is important to note that the same tray index is given to vapour and liquid variables passing each other on a tray.

The balances around a tray can be written as:

- total mass balance

\[ \frac{dM_j}{dt} = L_{j-1} + V_j - L_j - V_{j-1} \]  

(3.1)

- component mass balance

\[ \frac{d}{dt}(M_j x_{i,j}) = L_{j-1} x_{i,j-1} + V_j y_{i,j} - L_j x_{i,j} - V_{j-1} y_{i,j-1} \]  

(3.2)
energy balance

\[ \frac{d}{dt}(M_j H_j^L) = L_{j-1} H_{j-1}^L + V_j H_j^V - L_j H_j^L - V_{j-1} H_{j-1}^V \]  (3.3)

vapour-liquid relationship

\[ y_{i,j-1} = y(x_{i,j}, T_j^L) \]  (3.4)

flow hydraulics equation

\[ M_j = f(L_j) \]  (3.5)

bubble-point relation

\[ \sum_{i=1}^{n_a} y(x_{i,j}, T_j^L) = 1 \]  (3.6)

Assuming that the variables \( x, y, L, V, M, \) and \( T \) are continuous functions of the spatial variable \( z_r \) one can expand them using a Taylor series expansion.
Chapter 3 - Reduced-Order Models Based on the Orthogonal Collocation Method

Writing down only the first-order terms, the expansion of the liquid mole fraction is:

\[ x_{i,j-1} = x_{i,j} - \frac{\partial x_{i,j}}{\partial z_R} \Delta z_R \]  \hspace{1cm} (3.7)

where \( \Delta z_R \) is the spacing between consecutive trays.

When expressions similar to equation (3.7) are substituted into equations (3.1) to (3.5) one generates a first-order approximation, expressed by the following set of equations:

\[ \frac{\partial}{\partial t} (\tilde{M}x_i) = \frac{\partial}{\partial z_R} (V y_i - L x_i) \]  \hspace{1cm} (3.8)

\[ \frac{\partial \tilde{M}}{\partial t} = \frac{\partial}{\partial z_R} (V - L) \]  \hspace{1cm} (3.9)

\[ \frac{\partial}{\partial t} (\tilde{M}H^L) = \frac{\partial}{\partial z_R} (VH^V - LH^L) \]  \hspace{1cm} (3.10)

\[ y_i - \Delta z_R \frac{\partial y_i}{\partial z_R} = y(x_i, T^L) \]  \hspace{1cm} (3.11)

\[ \tilde{M} \Delta z_R = f(L) \]  \hspace{1cm} (3.12)

noting that in the previous equations \( M_j = \tilde{M} \Delta z_R \).

Substituting equation (3.9) into equations (3.8) and (3.10)

\[ \tilde{M} \frac{\partial x_i}{\partial t} = \frac{\partial}{\partial z_R} (V y_i - L x_i) - x_i \frac{\partial}{\partial z_R} (V - L) \]  \hspace{1cm} (3.13)

\[ \tilde{M} \frac{\partial H^L}{\partial t} = \frac{\partial}{\partial z_R} (VH^V - LH^L) - H^L \frac{\partial}{\partial z_R} (V - L) \]  \hspace{1cm} (3.14)

The set of equations (3.9), (3.11) to (3.14) must be solved subject to the following boundary conditions.
Chapter 3 - Reduced-Order Models Based on the Orthogonal Collocation Method

\[ x_{i,0}^1 |_{z = 0} = x_{i,0} \quad (3.15) \]
\[ L_{z = 0} = L_0 \quad (3.16) \]
\[ T^I_{z = 0} = T^I_0 \quad (3.17) \]
\[ y_{i,N_\tau} |_{z = N_\tau, \Delta z_R} = y_{i,N_\tau} \quad (3.18) \]
\[ \mathcal{V}_{z = N_\tau, \Delta z_R} = \mathcal{V}_{N_\tau} \quad (3.19) \]
\[ T^V_{z = N_\tau, \Delta z_R} = T^V_{N_\tau} \quad (3.20) \]

Of course it is impossible to solve analytically this system of partial differential equations. Cho and Joseph (1983a, 1983b) looked for numerical solutions by discretization of the space and time variables. The spatial variable was discretized using the orthogonal collocation procedure leading to the following system of differential and algebraic equations:

\[ \dot{M}_j \frac{d x_{i,j}}{d t} = \sum_{k=1}^{n+2} A_{j,k} (V_k y_{i,k} - L_k x_{i,k}) - x_{i,j} \sum_{k=1}^{n+2} A_{j,k} (V_k - L_k) \quad (3.21) \]

for \( j = 2,3,\cdots,n+2 \)

\[ \frac{d \dot{M}_j}{d t} = \sum_{k=1}^{n+2} A_{j,k} (V_k - L_k) \quad (3.22) \]

for \( j = 2,3,\cdots,n+2 \)

\[ \dot{M}_j \frac{d H^l_j}{d t} = \sum_{k=1}^{n+2} A_{j,k} (V_k H^l_k - L_k H^l_k) - H^l_j \sum_{k=1}^{n+2} A_{j,k} (V_k - L_k) \quad (3.23) \]

for \( j = 2,3,\cdots,n+2 \)

\[ \dot{M}_j \Delta z_R = f(L_j) \quad (3.24) \]

for \( j = 2,3,\cdots,n+2 \)

\[ y_{i,j} - \Delta z_R \sum_{k=1}^{n+2} A_{j,k} y_{i,k} = y(x_{i,j}, T^l_j) \quad (3.25) \]

for \( j = 1,2,\cdots,n+1 \)
\[ \sum_{i=1}^{na} y(x_i, T^L_i) = 1 \]  
for \( 0 \leq z_r \leq 1 \)

Equations (3.21) to (3.26) are subject to the following boundary conditions:

\[ x_{i,1} = x_{i,0} \]  
(3.27)

\[ L_1 = L_0 \]  
(3.28)

\[ T^L_1 = T^L_0 \]  
(3.29)

\[ y_{i,n+2} = y_{i,N_T} \]  
(3.30)

\[ V_{n+2} = V_{N_T} \]  
(3.31)

\[ T^V_{n+2} = T^V_{N_T} \]  
(3.32)

It should be stressed that despite equation (3.23) being written as a differential equation in time, it is not an independent equation. Following a procedure presented by Howard (1970), Cho and Joseph (1983b) reduced equation (3.23) to the set of algebraic equations that follows.

\[
\sum_{k=1}^{n+1} A_{j,k} \left( \sum_{i=1}^{c} \partial_{i,j} y_{i,k} + H^y_{k} - \chi_j \right) V_k = \sum_{k=1}^{n+2} A_{j,k} \left( \sum_{i=1}^{c} \partial_{i,j} x_{i,k} + H^L_{k} - \chi_j \right) L_k - A_{j,n+2} \left( \sum_{i=1}^{c} \partial_{i,j} y_{i,n+2} + H^y_{n+2} - \chi_j \right) V_{n+2}
\]

for \( j = 2, 3, \ldots, n + 2 \)

and where

\[ \partial_{i,j} = \frac{\partial H^y_i / \partial T}{\sum_{i=1}^{c} x_{i,j}} K_{i,j} - \frac{\partial H^L_j}{\partial x_{i,j}} \]  
(3.34)

\[ \chi_j = \sum_{i=1}^{c} \partial_{i,j} x_{i,j} + H^L_j \]  
(3.35)
The model formed by equations (3.21)-(3.22) and (3.24)-(3.33) is reduced to a set of equations in the state variables $x$ and $L$ evaluated at the collocation points $z_{R_i} (j = 2,3,\ldots,n+2)$. Equations (3.22) and (3.24) can be combined to produce:

$$\frac{dL_j}{dt} = \frac{\Delta z_{R_j}}{\left(\frac{\partial f}{\partial L_j}\right)} \left(\frac{dM_j}{dt}\right) = \frac{\Delta z_{R_j}}{\left(\frac{\partial f}{\partial L_j}\right)} \sum_{k=1}^{n+2} A_{j,k} (V_k - L_k)$$

(3.36)

The discretization of the time variable was carried out using a semi-implicit second-order Runge-Kutta algorithm.

Despite the good accuracy of the method in predicting both steady state and dynamic responses it suffers from the limitation that it only works for columns with no intermediate feed or sidedraw.

Cho and Joseph (1984) tried to tackle the problem of discontinuities in column profiles (introduced by feeds and sidedraws) by redefinition of variables. This procedure allowed them to fit the column profiles with a single polynomial across the entire column. This attempt was not very successful mainly because the discontinuities were not accounted for at the exact feed location but only at the collocation point located nearest to the feed location.

Stewart et al. (1985) devised a new form of orthogonal collocation for the simulation of large modular sequences of staged processes. In their approach a fractionation system is represented by a set of multistage modules linked to condensers, reboilers, feed and product lines. These links are expressed through the states and flowrates at the boundaries of the modules and they must attend the mass and energy balances on both sides of the boundaries. They showed that better results as well as more reliable reduced-order models are obtained if the orthogonal polynomials used are discrete ones (the best polynomial family is Hahn's polynomials).

Srivastava and Joseph (1985) addressed the importance of the number of
collocation points as well as their location. They define an order reduction parameter (ORP) that can be evaluated from a known steady state composition profile. The ORP enables one to specify a priori the number of collocation points needed for a given precision. In the examples they have studied they did not find much difference in the performance when using Hahn polynomials or Jacobi polynomials.

The problem of intermediate feeds and/or sidestreams was revisited by Srivastava and Joseph (1987a). They emphasised that the presence of feeds or sidedraws introduces two types of discontinuities in the column profiles. Assuming a total liquid feed introduced to the column at a tray located at a height \( z_f \) the discontinuities can be expressed as:

\[
L(z_i^-) \neq L(z_i^+) \tag{3.37}
\]

\[
\frac{dL}{dz_R}
\bigg|_{z_i^-} \neq \frac{dL}{dz_R}
\bigg|_{z_i^+} \tag{3.38}
\]

An alternative spline-fitting approach is presented to address the problem. One collocation point is placed right at the feed location and then the complete profile is approximated by splines. This can be exemplified for the liquid component flowrate profiles that would be

\[
Lx(z_R) = P_1(z_R) \quad 0 \leq z_R \leq z_f \tag{3.39}
\]

\[
Lx(z_R) = P_2(z_R) \quad z_f \leq z_R \leq 1.0 \tag{3.40}
\]

\[
P_1(z_f) = P_2(z_f) - Fx_f \tag{3.41}
\]

where \( P_1 \) and \( P_2 \) are polynomials.

According to their results this new approach leads to a large reduction in order of the reduced-order model keeping good accuracy, especially for columns with multiple feeds and sidestreams.

Srivastava and Joseph (1987b) tackled the problem of columns with steep and
flat composition profiles that are characteristic for the non-key components in a multicomponent system. Columns with steep and flat composition profiles exhibit high values of the order reduction parameter and hence require a great number of collocation points to approximate them.

In this new procedure the components in the column are divided into three categories and the composition profiles of each category are fitted by specially tailored polynomials. The possible categories are:

- components without flat and steep composition profiles - they are approximated using the normal reduction procedure;
- light components with steep composition profiles - the composition profile of these components changes rapidly in the top of the column and remains nearly constant over most of the stages in the column. The profile is then divided in two sections, one where the profile is assumed to be constant and the top section, where the profile is changing rapidly, is approximated by a polynomial of small degree;
- heavy components with steep composition profile - the composition profile of these components remains nearly constant over most of the stages in the column and changes rapidly near the bottom of the column. Such composition profiles are treated in a similar way as the light component profiles, but with a constant section and a small degree polynomial to fit the bottom section where the rapid changes are occurring.

There is a need for different sets of collocation points to approximate the profiles in the column.

The **global collocation points** are used to approximate the composition profiles that are not steep, the temperature profile, the liquid and vapour flowrate profiles.

The **local collocation points** are used to approximate the steep and flat composition profiles. The composition profile of each component in this
category will be approximated by a local polynomial of a different degree depending upon its ORP value and also the location where its profile can be considered constant.

The model equations at the global points and at the local points are coupled, meaning that the values of the state variables generated at the global points will be needed at the local point and vice versa. This can be done by means of a polynomial interpolation block that transfers the required information back and forth as desired during the simulation.

The new procedure is more complex than the original one as well as less general but, on the other hand, there is an overall reduction in the number of equations of the model and in the amount of computer time spent in the simulation.

Following the main ideas presented by Stewart et al. (1985) Pinto and Biscaia Jr (1988) developed new reduction strategies. In their approach only the temperature, liquid and vapour compositions are approximated by polynomial functions. In this way they can use the same node points for all the components and temperature because any discontinuity in the profiles involves only small changes in the compositions or in the temperature in the column profiles.

On the basis of their examples they recommended the utilisation of the sectional orthogonal collocation without extrapolation to simulate distillation columns. In this strategy the variables \(x\), \(y\) and \(T\) are approximated by different polynomials in each section of the column. The extremes of each section plus \(n\) internal collocation points are taken as interpolation points, and therefore the polynomials of each section meet on the feed plate.

The main differences between this new strategy and the one presented by Stewart et al. (1985) are:

- the extreme points in a section are used as interpolation and collocation points;
• the interpolating polynomials use the same node points, simplifying the programming of the model;
• the weights for the generation of the polynomials are neither Hahn's nor Jacobi's.

With these alterations they were able to obtain results that are equivalent or more precise (when compared with the rigorous solution) than those reported by Stewart et al. (1985).

Some interesting applications of the reduced-order models based on the orthogonal collocation procedure can be found in the literature. Drozdowicz and Martínez (1988) considered the use of a reduced-order model to be incorporated in a real-time simulator capable to simulate abnormal operation or the operation under failure. They developed an adaptive collocation scheme to enable them to follow the 'perturbation front' moving along the column during the transient. Seferlis and Hrymak (1994) presented some studies in the optimisation of distillation units comparing their results with those produced using a tray-by-tray model. The model developed by them was based on the technique of orthogonal collocation on finite elements [Finlayson (1980)].

A completely new approach was introduced by Huss and Westerberg (1994) leading to a very flexible model. They also used orthogonal collocation on finite elements in their model but the key point in their development lies in the transformation of two variables. An exponential transformation on the tray number allowed them to accurately simulate a large column section (even with an infinite number of trays!) with a small number of collocation points. As they properly stress, there are some problems when using polynomials to represent sharp splits. When the mole fractions of the components approach zero (or one) the polynomial creates a curved trajectory, 'bouncing' off the boundary. A hyperbolic tangent transformation on the mole fractions was introduced to eliminate this problem. Now, as the mole fraction approaches zero or one, the transformed variable goes to negative infinity and plus infinity, respectively. This may cause some problems for very small mole fractions but it does allow
an asymptotic approach to the boundary. They report very interesting applications of this new strategy on the design and optimisation of new columns and in the simulation of minimum reflux conditions.

### 3.3- Packed Columns

The utilisation of the orthogonal collocation method on the order reduction of models for packed separation columns was first presented in the literature by Srivastava and Joseph (1984).

Considering the pressure drop through the bed to be negligible, the holdup of the vapour phase to be small in comparison with the liquid phase and using the two-film theory of mass transfer, Srivastava and Joseph (1984) were able to write material balance equations for a packed separation column as follows (see Figures 3.2 and 3.3 for notation):

**Figure 3.2. Two film model of a packed column**

- overall mass balance

\[
\frac{\partial H_R}{\partial t} = \frac{\partial L}{\partial z_R} \frac{\partial V}{\partial z_R} \tag{3.42}
\]
Figure 3.3. Rectification section of a distillation column with a total condenser

- overall vapour phase balance

\[
0 = -\frac{\partial V}{\partial z_R} - \sum_{k=1}^{\infty} N_k
\]  

(3.43)

- overall component balance

\[
\frac{\partial}{\partial t} (H_R x_k) = \frac{\partial}{\partial z_R} (L x_k) - \frac{\partial}{\partial z_R} (V y_k)
\]  

\[ k = 1, 2, \cdots, nc \]  

(3.44)

- vapour phase component balance

\[
0 = -\frac{\partial}{\partial z_R} (V y_k) - N_k
\]  

\[ k = 1, 2, \cdots, nc \]  

(3.45)
• overall enthalpy balance
\[ \frac{\partial}{\partial t}(H_R H^L) = -\frac{\partial}{\partial Z_R}(L H^L) - \frac{\partial}{\partial Z_R}(V H^V) \]  
(3.46)

• enthalpy balance over the vapour phase
\[ 0 = -\frac{\partial}{\partial Z_R}(V H^V) - Q^V - q^V \]  
(3.47)

where
\[ Q^V = \sum_{k=1}^{nc} N_k \overline{H}_k^V \]  
(3.48)
\[ q^V = h^V a_e (T^V - T_i)(A_i) \]  
(3.49)

• enthalpy balance over the interface
\[ Q^V + q^V = Q^L + q^L \]  
(3.50)

where
\[ Q^L = \sum_{k=1}^{nc} N_k \overline{H}_k^L \]  
(3.51)
\[ q^L = h^L a_e (T_i - T_i)(A_i) \]  
(3.52)

In their work the interface mass transfer was expressed by the following equation:
\[ N_k = (K_{OG} a_e)(y_k - y_k^i)(A_i) \]  
(3.53)
\[ k = 1,2,\cdots, nc \]

The set of equations formed by equations (3.42) to (3.46) and (3.50) must be solved subject to the following boundary conditions (considering a rectification section with a total condenser - Figure 3.3):
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\[ L_{\mid z_R = z_R} = L_{n+2} \]  
(3.54)

\[ T^L_{\mid z_R = z_R} = T^L_{n+2} \]  
(3.55)

\[ x_{i\mid z_R = z_R} = y_{i\mid z_R = z_R} \]  
(3.56)

\[ V_{\mid z_R = 0} = V_1 \]  
(3.57)

\[ T^V_{\mid z_R = 0} = T^V_1 \]  
(3.58)

\[ y_{i\mid z_R = 0} = y_{i,1} \]  
(3.59)

The solution to this system of partial differential equations is achieved by discretization of the space and time variables. The space variable was discretized using the method of orthogonal collocation leading to the following set of ordinary differential equations:

\[ \frac{dH_{Rj}}{dt} = \sum_{k=1}^{n+2} A_{j,k} L_k - \sum_{k=1}^{n+2} A_{j,k} V_k \]  
(3.60)

Normally the liquid holdup in the packing is a known function of the liquid flow rate,

\[ H_{Rj} = f(L_j) \]  
(3.61)

\[ \frac{dH_{Rj}}{dt} = f'(L_j) \frac{dL_j}{dt} \]  
(3.62)

Therefore equation (3.60) can be written as

\[ \frac{dL_j}{dt} = \frac{1}{f'(L_j)} \left[ \sum_{k=1}^{n+2} A_{j,k} L_k - \sum_{k=1}^{n+2} A_{j,k} V_k \right] \]  
(3.63)

\[ j = 1, 2, \ldots, n + 1 \]

\[ \frac{d}{dt} (H_{Rj} x_{i,j}) = \sum_{k=1}^{n+2} A_{j,k} L_k x_{i,j} - \sum_{k=1}^{n+2} A_{j,k} V_k y_{i,j} \]  
(3.64)

\[ j = 1, 2, \ldots, n + 1 \quad i = 1, 2, \ldots, nc \]
Chapter 3 - Reduced-Order Models Based on the Orthogonal Collocation Method

\[ 0 = -\sum_{k=1}^{n+2} A_{j,k} y_{l,j} - N_{l,j} \quad (3.65) \]

\[ j = 2,3,\ldots,n+2 \quad i = 1,2,\ldots,nc \]

\[ \frac{d}{dt}(H_j H_j) = \sum_{k=1}^{n+2} A_{j,k} L_k H_k^L - \sum_{k=1}^{n+2} A_{j,k} V_k H_k^V \quad (3.66) \]

\[ j = 1,2,\ldots,n+1 \]

\[ 0 = -\sum_{k=1}^{n+2} A_{j,k} V_k H_k^V - h_y a_y A_y (T_j^V - T_j^L) - \sum_{l=1}^{nc} N_{l,j} H_{l,j}^V \quad (3.67) \]

\[ j = 2,3,\ldots,n+2 \]

Now the boundary conditions to be satisfied are:

\[ L|_{z R = z_{n+2}} = L_{n+2} \quad (3.68) \]

\[ T^L|_{z R = z_{n+2}} = T^L_{n+2} \quad (3.69) \]

\[ x|_{z R = z_{n+2}} = x_{n+2} \quad (3.70) \]

\[ V|_{z R = 0} = V_1 \quad (3.71) \]

\[ T^V|_{z R = 0} = T^V_1 \quad (3.72) \]

\[ y|_{z R = 0} = y_1 \quad (3.73) \]

The overall enthalpy balance [equation (3.66)] can be reduced to an algebraic equation adopting a similar procedure to that presented in equations (3.33) to (3.35).

Using the model represented by the set of equations above Srivastava and Joseph (1984) simulated some multicomponent distillation and absorption columns. The integration in time was accomplished using a semi-implicit Runge-Kutta integration method and the agreement between steady state calculated and reported values were good. No comparison between dynamic results was presented.
Wang and Cameron (1991) extended the approach presented by Srivastava and Joseph (1984) to include the possibility to simulate a complete column with intermediate feeds and/or sidestreams. They also introduced in the model a simple hydrodynamic equation for packed columns developed by Jiřičný and Staněk (1990).

Wang and Cameron (1991) simulated an industrial depropanizer that uses a Mellapak 250Y structured packing. It is important to stress that the mass and heat transfer coefficients they used were evaluated using a more rigorous procedure than the one adopted by Srivastava and Joseph (1984). The mass transfer coefficients for binary systems were determined either using the Onda correlation [see equation (5.75)] or the Spiegel and Meier correlation [Spiegel and Meier (1987)] written as follows:

\[
\kappa_{i,j}^v = K_s \frac{d_{i,j}^v}{d_p} \left( \frac{d_p G}{\eta_v} \right)^{0.8} \left( \frac{\eta_v}{\rho_v d_{i,j}^v} \right)^{1.3}
\]

(3.74)

with \(K_s\) in the range 0.018 to 0.040.

For the computation of an effective mass transfer coefficient for a component in the multicomponent system an equation suggested by Wilke was used (1950)

\[
(K_{OG})_i = \frac{1 - y_i}{\sum_{j=1}^{nc} y_j / c_j^v \kappa_{i,j}^v}
\]

(3.75)

The vapour phase heat transfer coefficient was approximated by using a Chilton-Colburn type analogy:

\[
h^v = K_{OG} \bar{C}_{pm}^v (Le^v)^{2/3}
\]

(3.76)

In their studies the vapour phase mass and heat transfer coefficients were affected not only by the vapour flowrates but also by the temperature and compositions. Since the widely used simplified one variable correlations gave
poor approximations they concluded that the rigorous computations of mass and energy transfer coefficients and liquid holdup based on the physicochemical properties of the streams are essential to the entire study of packed column dynamics. Their results indicate, as expected, that the fluid dynamics are much faster than the composition transients.

Wardle and Hapoglu (1992) solved the same example problem presented by von Rosenberg and Hadi (1980) but, instead of using a polynomial approximation in the solution of the equations of the model as Srivastava and Joseph (1984) did, they opted for employing the technique of orthogonal collocation on finite elements [Finlayson (1980)]. They obtained a very close agreement with the results obtained using the finite difference scheme as proposed by von Rosenberg and Hadi (1980) but the orthogonal collocation on finite elements approach requires far fewer discretization points. Some polynomial families were tested (Jacobi, Legendre and cubic Hermite) leading to the same results but requiring different CPU times. When more than three collocation points are required the cubic Hermite polynomial leads to a smaller number of equations (less CPU time) because continuity relationships are not required. Wardle and Hapoglu (1992) employed the same simplified correlations for evaluation of the overall mass transfer coefficient that were presented by von Rosenberg and Hadi (1980).

There are in the open literature some references to the application of the reduced order models originated by the utilisation of the method of orthogonal collocation to some control studies. Karlström and Breitholtz (1990) obtained a linearised large state space model that was further reduced by means of the optimal Hankel norm method. The dynamic results obtained using this model are compared with experimental data for a binary system in a full scale industrial distillation column with structured packing. They reported good agreement between experimental and simulated data.

Wang and Cameron (1992) introduced some simplifications (e.g., considered a binary system, approximated $K_{OG}$ as a pointwise linear function of $V$,
approximated \( H_R \) as a pointwise linear function of \( L \), etc.) in the model previously presented by Wang and Cameron (1991) in order to develop some optimal control studies. They concluded that the model provides a good basis to carry out optimal control studies but recommended the investigation of more rigorous methods for the computation of mass and heat transfer rates.

3.4- CONCLUSIONS

From the results reported in the literature it is clear that the orthogonal collocation technique is a powerful option for the order reduction of the models for separation columns.

Almost all the performance comparisons of the reduced-order models have been made against ‘rigorous’ models based on the equilibrium stage concept and/or with the interphase mass transfer rates evaluated in a simplified way. The reduced-order models were developed on the same basis.

It would be worthwhile to develop reduced-order models based on the nonequilibrium stage concept as well as to incorporate in the model some of the rigorous matricial methods for the computation of the interphase mass transfer rates.

This is the chosen direction and a review on the rigorous treatment of multicomponent mass transfer is presented in the following chapter.
4- MULTICOMPONENT MASS TRANSFER

4.1- INTRODUCTION

When dealing with the problem of designing a new separation process a chemical engineer will normally be looking at concentrated systems involving the simultaneous diffusion of several components as well as simultaneous heat transfer.

The most traditional approaches to solve the problem above assume that the diffusion flux of a component in a multicomponent mixture is a function of its concentration gradient only. It is also assumed that the heat flux depends only on the temperature gradient. There are few situations of practical relevance where these simplifications are strictly correct.

During the last two decades it was proved without doubt that multicomponent systems can display transport characteristics completely different from those of a binary nature. Several different formulations (rigorous and approximate) to tackle the problem of simultaneous mass and heat transfer in multicomponent systems were developed [Krishna and Standart (1979)].

In this chapter a review on these different formulations is presented. Greater emphasis is given to the methods that are going to be incorporated in the reduced order models for separation processes to be presented on Chapters 6, 7 and 8.

In the first part of the chapter [sections 4.2 to 4.5] the basic equations to analyse multicomponent mass transfer processes are presented. In section 4.6 a number of different solutions (exact and approximate) to these equations, based on the film model to describe the multicomponent mass and heat transfer, is presented. Finally, in section 4.6.7, some brief comments are made on the applicability of the methods presented in this chapter.
4.2 - The Maxwell-Stefan Equations

The starting point for a rigorous treatment of the diffusion in a system with \( nc \) components may be the Maxwell-Stefan equations [Taylor and Krishna (1993)] that can be expressed as:

\[
d_i = \sum_{j=1}^{nc} \left( y_i N_j - y_j N_i \right) \frac{c_i^y D_{i,j}}{c_j^y D_{j,i}} = \sum_{j=1}^{nc} \left( y_i J_j - y_j J_i \right) \frac{c_i^y D_{i,j}}{c_j^y D_{j,i}}
\]  

(4.1)

where the diffusion fluxes, \( J_i \), are functions of the Maxwell-Stefan diffusivity, \( D_{i,j} \), and \( d_i \) is the driving force for the diffusion of component \( i \) in a multicomponent mixture at constant temperature and pressure.

4.2.1 - Ideal Gas Mixtures

When dealing with ideal gas mixtures one can express the driving force for the diffusion of component \( i \) as:

\[
d_i = \left( \frac{1}{P} \right) \nabla p_i
\]

(4.2)

In all the situations to be analysed in this work the system pressure will be considered constant along the diffusion path. This will allow us to rewrite equation (4.1) combined with equation (4.2) as:

\[
\nabla y_i = \sum_{j=1}^{nc} \left( y_i N_j - y_j N_i \right) \frac{c_i^y D_{i,j}}{c_j^y D_{j,i}} = \sum_{j=1}^{nc} \left( y_i J_j - y_j J_i \right) \frac{c_i^y D_{i,j}}{c_j^y D_{j,i}}
\]

(4.3)

It is important to stress that only \( nc-1 \) equations (4.3) are independent since the summation of the component gradients equals zero (\( \sum_{i=1}^{nc} \nabla y_i = 0 \)).

Equations (4.3) are more useful when written in a matricial form (dimension \( nc-1 \)) as:

\[
(J) = -c_i^y [B]^{-1} (\nabla y)
\]

(4.4)
with the elements of matrix $B$ defined by

$$B_{ij} = \frac{y_i}{B_{i,nc}} + \sum_{k=1}^{nc} \frac{y_k}{B_{i,k}}$$

(4.5)

$$B_{i,j} = -y_i \left( \frac{1}{B_{i,j}} - \frac{1}{B_{i,nc}} \right)$$

(4.6)

### 4.2.2- Nonideal Fluids

When analysing the diffusion in nonideal fluids the driving force $d_i$ will be defined by

$$d_i = \frac{x_i}{RT} \nabla_{T,P} \mu_i$$

(4.7)

As with the ideal gas analysis, the sum of the $nc$ driving forces equals zero, therefore only $nc-1$ equations (4.1) are independent.

To avoid dealing with chemical potential gradients when analysing the diffusion of nonideal liquids the driving force will be expressed employing mole fraction gradients instead.

$$d_i = \sum_{j=1}^{nc-1} \Gamma_{i,j} \nabla x_j$$

(4.8)

where

$$\Gamma_{i,j} = \delta_{i,j} + x_i \left. \frac{\partial \ln y_i}{\partial x_j} \right|_{T,P,\Sigma}$$

(4.9)

and where $\Sigma$ indicates that the derivatives must be evaluated keeping constant all the mole fractions but that of components $j$ and $nc$. To correct for deviations from ideal gas behaviour when working with dense gas mixtures the activity coefficient in equation (4.9) can be replaced by the fugacity coefficient.
For the nonideal case the result of the combination of equations (4.1) and (4.8), cast in a \( nc-1 \) dimensional matrix form, is

\[
\begin{pmatrix} \mathbf{J} \end{pmatrix} = -c_i^l [B]^{-1} [\Gamma] [\nabla \mathbf{x}] \tag{4.10}
\]

### 4.3- Fick’s Law for Multicomponent Systems

The analysis of diffusion in binary mixtures led Adolf Fick to establish in the late 1800's that molecular diffusion is proportional to the decrease in the concentration gradient \([\text{Henley & Seader (1981)}]\). The molar flux of component 1 can be calculated using one of the forms of his 'law':

\[
\mathbf{J}_1 = -c_i^l D_{1,2} \nabla x_1 \tag{4.11}
\]

Equation (4.11) can be seen as the definition of the Fick diffusion coefficient. Since the sum of the diffusion fluxes, \( \mathbf{J}_1 \) and \( \mathbf{J}_2 \), is zero and the summation of the mole fractions, \( x_1 \) and \( x_2 \), is equal to unity, it follows from equation (4.11) that \( D_{1,2} = D_{2,1} \).

The generalisation of equation (4.11) to encompass diffusion in a system with \( nc \) components is given by equation (4.12).

\[
\mathbf{J}_j = -c_i^l \sum_{k=1}^{nc-1} D_{j,k} \nabla x_k \tag{4.12}
\]

The matricial form (dimension \( nc-1 \)) of equation (4.12) is

\[
\begin{pmatrix} \mathbf{J} \end{pmatrix} = -c_i^l [D] [\nabla \mathbf{x}] \tag{4.13}
\]

### 4.4- Interaction Effects

It is clear from the generalised Fick’s law [equation (4.13)] that the existence of nonzero cross-coefficients (or off diagonal elements) in the Fickian matrix \([D]\) will allow the multicomponent systems to have a behaviour quite different from the binary systems.
Toor (1957) investigated this different behaviour of multicomponent systems showing that it is possible to have a diffusion flux of one component even in the absence of a composition gradient for this component (osmotic diffusion). The phenomenon known as diffusion barrier will happen when, despite the presence of a composition gradient of a component, this component does not diffuse at all. It is also possible for a component to diffuse against its own composition gradient, a condition known as reverse diffusion.

Taylor and Krishna (1993) presented a picture where these effects are easily observed. In Figure 4.1 the diffusion flux of component 1 was plotted against the negative of its composition gradient. For binary systems the line representing Fick’s law passes through the origin [Figure 4.1(a)] but this may not happen in a multicomponent system. The general rule for multicomponent systems is to have an intercept different from zero (either positive or negative) leading to the situation where the interaction effects described in the previous paragraph may occur [Figure 4.1(b)].

Figure 4.1. Interaction effects on diffusion in multicomponent systems [adapted from Taylor and Krishna (1993)].
It must be clear that in the regions labelled 'normal' diffusion behaviour the diffusion flux of component 1 may be affected by the composition gradients of the other components.

### 4.5- DIFFUSION COEFFICIENTS

#### 4.5.1- Binary Mixtures

Writing down the Maxwell-Stefan equation (4.10) for a binary mixture as

\[ J_i = -c_i B^{-1} \Gamma \nabla x_i = -c_i B_{12} \Gamma \nabla x_1 \]

(4.14)

and comparing it with Fick's 'law', equation (4.11), one can get the relationship between the Fickian diffusion coefficient and the Maxwell-Stefan diffusivity for a binary mixture as:

\[ D_{12} = B^{-1} \Gamma = B_{12} \Gamma \]

(4.15)

For ideal systems the two diffusion coefficients are the same since \( \Gamma \) becomes equal to unity.

There are several methods for the estimation of the binary diffusion coefficients in binary gas mixtures [Reid et al. (1987)]. The reader is directed to Chapter 5 where the matter is further discussed.

Some extra care must be taken when estimating the binary diffusion coefficients for liquid mixtures because they can be strongly affected by the mixture composition. Normally the estimation is made in two steps: first the infinite dilution diffusion coefficients are calculated and secondly they are combined to take into account the mixture composition.

When one of the mole fractions approaches unity the thermodynamic factor \( \Gamma \) also tends to unity and the two diffusivities become equal to what is known as the infinite dilution diffusion coefficient (e.g., \( D_{12}^0 \) is the diffusion coefficient of
component 1 infinitely diluted in solvent 2). In Chapter 5 the method used in
this work for the evaluation of the infinite dilution diffusion coefficients will be
presented.

There are in the literature many methods to predict the composition
dependence of the Maxwell-Stefan diffusion coefficients in binary systems.
Reid et al. (1987) recommend the procedure presented by Vignes (1966) and
that is given in the following equation.

\[ B_{12} = (C_{12}^0)^{x_2} (C_{21}^0)^{x_1} \]  \hspace{1cm} (4.16)

### 4.5.2- Multicomponent Mixtures

The comparison of equations (4.10) and (4.13) allows us to obtain a
relationship between the Fick diffusion coefficients and the Maxwell-Stefan
diffusion coefficients expressed as

\[ [D] = [B]^{-1} [\Gamma] \] \hspace{1cm} (4.17)

Equation (4.17) states the equivalence of matrices \([D]\) and \([B]^{-1} [\Gamma]\) but not
their equality. The only way to relate the Fickian diffusion coefficients with the
Maxwell-Stefan diffusion coefficients is to assume the equality of these two
matrices [Taylor and Krishna (1993)], therefore writing:

\[ [D] = [B]^{-1} [\Gamma] \] \hspace{1cm} (4.18)

Now, knowing the values of the binary Maxwell-Stefan diffusivities and the
matrix of thermodynamic factors, one can predict the matrix of Fickian diffusion
coefficients [using equations (4.5), (4.6), (4.9) and (4.18)].

For ideal systems, where the matrix of thermodynamic factors becomes the
identity matrix, equation (4.18) simplifies to

\[ [D] = [B]^{-1} \] \hspace{1cm} (4.19)
As can be easily concluded by the observation of equations (4.5), (4.6) and (4.19), depending on the component numbering one will produce quite different matrices of Fickian diffusion coefficients, \([D]\). Taylor (1981) showed that despite the differences in the matrices, their eigenvalues are the same and, more importantly, for a given set of driving forces they will produce the same set of fluxes.

There is still the problem of taking into account the effect of the mixture composition in the multicomponent Maxwell-Stefan diffusion coefficients. To tackle this problem Kooijman and Taylor (1991) presented a generalisation of the Vignes equation [equation (4.16)] and their final expression is given below.

\[
B_{ij} = \left( B_{ij}^0 \right)^{x_j} \left( B_{jj}^0 \right)^{x_i} \prod_{k=1, k \neq i, j}^{n_c} \left( B_{ik}^0 B_{jk}^0 \right)^{x_k/2}
\]  

(4.20)

### 4.6- INTERPHASE MASS TRANSFER

One is normally interested in the evaluation of the fluxes across the interface between two adjacent phases. For example, in distillation, one is concerned with the computation of the fluxes of the various components across the vapour-liquid interface. This section will present some alternatives for the solution of this problem based on the film model.

Initially an exact solution for an ideal gas mixture problem is presented in subsection 4.6.1.a. After presenting the definition of the mass transfer coefficients, this exact solution is rewritten in terms of them (subsection 4.6.3). Some approximations to the rigorous treatment are then presented in subsection 4.6.4. Subsection 4.6.5 is devoted to extend the ideas and procedures developed in the previous subsections to nonideal fluid mixtures. Following this, a discussion of how to extend the film theory to embrace simultaneous mass and heat transfer problems is presented in subsection 4.6.6. Finally, the section comes to a closure with some remarks on a statistical comparison of performance of the methods presented in this section.
Let us analyse the two phase system represented in Figure 4.2 where typical composition profiles are depicted. In the simple interface model most frequently used the interface mole fractions, \( x_i \) and \( y_i \), are considered to be in equilibrium. In the two phases the bulk mole fractions are denoted by \( x_i^c \) and \( y_i^c \).

![Figure 4.2. Mole fractions close to the interface during mass transfer](image)

### 4.6.1- The Film Theory

The final step in the evaluation of the required mass transfer rates across an interface is to solve the continuity equations together with equations describing the diffusion process and the boundary conditions of the problem. Although the basic differential equations describing the phenomena taking place at the interface are well known, the fluid flow pattern at the interface is so complicated that one must introduce several simplifications in order to be able to solve them.

The simplest, the oldest and, probably the most useful model for describing multicomponent mass (and heat) transfer across an interface is the film model [Krishna and Taylor (1986)].

In the film model all the resistance to mass transfer in turbulent flow is assumed to be concentrated in a thin film adjacent to the phase boundary. Inside this film the transfer is considered to be by steady state molecular diffusion and, outside the film there are no concentration gradients as they are eliminated by turbulent eddy mixing. Inside the film the mass transfer is essentially in the direction normal to the interface. In Figure 4.3 there is a pictorial representation of the
concentration profiles in the film model.

Figure 4.3. Interface region according to the film theory (film of thickness $t$).

4.6.1. A **exact solution of the Maxwell-Stefan equations**

Krishna and Standart (1976a) presented an exact matricial solution for the Maxwell-Stefan equations for a film model considering a mixture of ideal gases and their development is presented below.

Let us consider equation (4.3) written for unidimensional transfer

$$\frac{dy_i}{dz} = \sum_{j=1}^{n_c} \left( y_i N_j - y_j N_i \right) c_i^y D_{i,j}$$

(4.21)

Eliminating $y_{nc}$ from equation (4.21) and knowing that the summation of the mole fractions equals unity one can get

$$\frac{dy_i}{d\eta} = \Phi_i y_i + \sum_{j=1}^{n_c} \Phi_{i,j} y_j + \phi_i$$

(4.22)

The following variables were introduced in equation (4.22):
Chapter 4 - Multicomponent Mass Transfer

- \( \eta \), dimensionless distance

\[
\eta = \frac{Z - Z_0}{\ell} \tag{4.23}
\]

- the coefficients \( \Phi_{i,j} \)

\[
\Phi_{i,j} = \frac{N_i}{c_i^v D_{i,nc} / \ell} + \sum_{k \neq i}^{nc} \frac{N_k}{c_i^v D_{i,k} / \ell} \tag{4.24}
\]

\[
\Phi_{i,j} = -N_i \left( \frac{1}{c_i^v D_{i,j} / \ell} - \frac{1}{c_i^v D_{i,nc} / \ell} \right) \tag{4.25}
\]

- a mass transfer parameter, \( \phi \)

\[
\phi = -\frac{N_i}{c_i^v D_{i,nc} / \ell} \tag{4.26}
\]

Equation (4.22) can be written in a matricial form [dimension nc-1] as

\[
\frac{d(y)}{d\eta} = [\Phi](y) + (\phi) \tag{4.27}
\]

The set of linear differential equations with constant coefficients represented by equation (4.27) is subject to the boundary conditions of the film model, namely:

\[
y_i \big|_{\eta=0} = y_i \big|_{z=z_0} = y_{i,0} \tag{4.28}
\]

\[
y_i \big|_{\eta=1} = y_i \big|_{z=z_0} = y_{i,\delta} \tag{4.28}
\]

The solution of equation (4.27) is sought by a successive substitution scheme, also known as Picard’s method, as presented by Amundson (1966). Following this procedure, equation (4.27) is integrated after the separation of the variables resulting in an expression for the vector of mole fractions, \( (y) \), that is a function of an integral of \( (y) \) over the dimensionless position, \( \eta \). This solution is substituted into the integrand and the process is repeated indefinitely.
producing a solution that is a function of the *matrizant* [see section 4.6.5.a for the definition of the *matrizant*] of [\(\Phi\)]. As the *matrizant* of a constant matrix is equal to the exponential of this matrix, the final mole fraction profile is given by:

\[
(y - y_0) = \left[ \exp[\Phi] \eta - [I] \right] \left[ \exp[\Phi] - [I] \right]^{-1} (y_0 - y_0)
\]  

(4.29)

The diffusion fluxes can be calculated from equations (4.4), (4.13) and (4.23) as

\[
(J) = c_i^y \left[ B \right]^{-1} \frac{d(y)}{d\eta} = c_i^y \left[ D \right] \frac{d(y)}{d\eta}
\]  

(4.30)

When the mole fraction gradients obtained from equation (4.29) are introduced into equation (4.30) the following equations for the evaluation of the diffusion fluxes at the film boundaries are produced:

\[
(J_0) = c_i^y \left[ D_0 \right] \frac{d(y)}{d\eta} \bigg|_{\eta=0} = c_i^y \left[ D_0 \right] \left[ \exp[\Phi] - [I] \right]^{-1} (y_0 - y_\delta)
\]  

(4.31)

\[
(J_\delta) = c_i^y \left[ D_\delta \right] \frac{d(y)}{d\eta} \bigg|_{\eta=1} = c_i^y \left[ D_\delta \right] \left[ \exp[\Phi] \left[ \exp[\Phi] - [I] \right]^{-1} (y_0 - y_\delta)
\]  

(4.32)

**4.6.2- The Bootstrap Problem**

As already mentioned, even in situations where the diffusion fluxes, \(J_i\), are known, one cannot immediately calculate the molar fluxes, \(N_i\), because all \(nc\) of these fluxes are independent and only \(nc-1\) of the diffusion fluxes are independent. The evaluation of the molar fluxes knowing the diffusion fluxes is known in the literature as the bootstrap problem. Clearly there is a need for some more information to allow us to solve the bootstrap problem and this piece of information is normally obtained via the analysis of the context on which the particular mass transfer process is taking place.

In a general form the additional relationship between the molar fluxes can be
written as:

\[ \sum_{i=1}^{nc} v_i N_i = 0 \quad (4.33) \]

The \( v_i \) are known as the determinacy coefficients and one can get some idea on the values they assume in the examples listed on Table 4.1.

**Table 4.1. Determinacy coefficients [adapted from Smith and Taylor(1983)]**

<table>
<thead>
<tr>
<th>Mass transfer process</th>
<th>( v_i )</th>
<th>( v_{nc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equimolar counter transfer</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Diffusion through stagnant species</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Simultaneous heat and mass transfer</td>
<td>( H^V_i - H^L_i )</td>
<td>( H^V_{nc} - H^L_{nc} )</td>
</tr>
<tr>
<td>Zero mass average velocity</td>
<td>( M_i )</td>
<td>( M_{nc} )</td>
</tr>
</tbody>
</table>

The molar fluxes, \( N_i \), are related to the diffusion fluxes, \( J_i \), by

\[ N_i = J_i + x_i N_i \quad (4.34) \]

Combining equations (4.33) and (4.34) one can express the total molar flux, \( N_t \), in terms of the diffusion fluxes as:

\[ N_t = - \left( \sum_{i=1}^{nc} v_i J_i / \sum_{i=1}^{nc} v_i x_i \right) = - \sum_{k=1}^{nc-1} \Lambda_k J_k \quad (4.35) \]

where the elements of \( \Lambda_k \) are defined by

\[ \Lambda_k = \left( v_k - v_{nc} \right) / \sum_{j=1}^{nc} v_j x_j \quad (4.36) \]

and from equations (4.34) and (4.35) one gets the working expression for the evaluation of the molar fluxes from the diffusion fluxes as
\[ N_l = \sum_{k=1}^{nc-1} \beta_{i,k} J_k \]  
\hspace{1cm} (4.37)

where

\[ \beta_{i,k} = \delta_{i,k} - x_i \Lambda_k \]  
\hspace{1cm} (4.38)

and \( \delta_{i,k} \) is the Kronecker delta.

Equations (4.35) and (4.37) are more useful when cast in a \( nc-1 \) dimensional matrix form given by

\[ N_l = (\Lambda)^T (J) \]  
\hspace{1cm} (4.39)

and

\[ (N) = [\beta] (J) \]  
\hspace{1cm} (4.40)

4.6.3- Mass Transfer Coefficients

4.6.3.a- Binary mass transfer coefficients

Bird et al. (1960) defined a binary mass transfer coefficient as

\[ k_b = \lim_{N_l \to 0} \frac{N_{1,b} - x_{i,b} N_l}{c_i^L (x_{i,b} - x_{i,d})} = \lim_{N_l \to 0} \frac{J_{1,b}}{c_i^L \Delta x_i} \]  
\hspace{1cm} (4.41)

The coefficients defined in equation (4.41) are the so called low-flux or zero-flux coefficients and these are the coefficients that are usually available from correlations of mass transfer data. In those situations where one has a finite flux of the components across the interface this will cause distortions to the composition and velocity profiles. Therefore, the definition of the finite flux mass transfer coefficient is introduced as

\[ k_b^* = \frac{N_l - x_{i,b} N_l}{c_i^L \Delta x_i} = \frac{J_{1,b}}{c_i^L \Delta x_i} \]  
\hspace{1cm} (4.42)

The finite flux mass transfer coefficient is usually related to the low-flux mass
Chapter 4 - Multicomponent Mass Transfer

transfer coefficient via a correction factor, \( \Xi_b \), that accounts for the effects of the finite fluxes on \( k_b \).

\[
K_b^* = k_b \Xi_b \quad (4.43)
\]

4.6.3.b- Multicomponent mass transfer coefficients

Analogous to the development in the previous section a \( nc-1 \) dimensional matrix of finite flux mass transfer coefficients is defined as

\[
(J_b) = (N) - (x_b)N_i = c_i^s [k_b^*](x_b - x_i) = c_i^s [k_b^*](\Delta x) \quad (4.44)
\]

and the low-flux mass transfer coefficients are related to the finite flux mass transfer coefficients by way of a matrix of correction factors, \( [\Xi_b] \)

\[
[k_b^*] = [k_b] [\Xi_b] \quad (4.45)
\]

4.6.3.c- Overall mass transfer coefficients

Referring back to Figure 4.3 one notices that there should be continuity of the fluxes across the interface

\[
N_i^{phase x} = N_i^{phase y} = N_i \quad i = 1,2,\ldots, nc \quad (4.46)
\]

therefore one can express these fluxes using the driving forces on either side of the interface as

\[
(N) = c_i^s [k_i^{-1}](x_b - x_i) + N_i(x_b) = c_i^s [\beta_i] [k_i^{-1}](x_b - x_i) \quad (4.47)
\]

\[
(N) = c_i^v [k_i^{-1}](y_i - y_b) + N_i(y_b) = c_i^v [\beta_i] [k_i^{-1}](y_i - y_b) \quad (4.48)
\]

As already mentioned it is assumed that at the interface the two phases are in equilibrium and therefore related by

\[
y_i = K_i x_{i,1} \quad i = 1,2,\ldots, nc - 1 \quad (4.49)
\]
where the '\(K\) values' are frequently given by

\[
K_i = \gamma_i P_i^S / P
\]

(4.50)

In many situations it will be useful to have the vapour-liquid relationship linearised over the range of compositions encountered in the two phase region. Doing so one could write down the equilibrium relationship as

\[
(y_i) = [M](x_i) + (b)
\]

(4.51)

where the elements of the matrix \([M]\) are given by

\[
M_{i,j} = \frac{\partial y_i^*}{\partial x_j} \quad i, j = 1, 2, \ldots, nc - 1
\]

(4.52)

where \(y_i^*\) is the mole fraction of the vapour in equilibrium with a liquid of composition \(x_i\).

Considering an equilibrium relationship of the form of equation (4.50) the matrix \([M]\) can be computed as

\[
[M] = [K][\Gamma]
\]

(4.53)

with the matrix \([K]\) been a diagonal matrix with the first \(nc-1\) equilibrium ratios.

When dealing with binary mixtures the usual procedure is to combine the resistances to mass transfer in both phases obtaining an expression for the evaluation of the molar fluxes without the knowledge of the interface composition. Krishna and Standart (1976b) presented a matrix generalisation of these ideas for a multicomponent system and their result is

\[
(N) = c_i^V \left[\beta_v\right] \left[K_{ov}^*\right] (y_b - y_b^*)
\]

(4.54)

with the matrix of overall mass transfer coefficients defined as

\[
\left[K_{ov}^*\right]^{-1} \left[\beta_v\right]^{-1} = \left[k_{ov}\right]^{-1} \left[\beta_v\right]^{-1} + \frac{c_i^V}{c_i^{\text{L}}} [M] \left[k_{\text{L}}\right]^{-1} \left[\beta_{\text{L}}\right]^{-1}
\]

(4.55)
4.6.3.d - An exact solution of the Maxwell-Stefan equations - Mass transfer coefficients formulation

The exact solution presented in section 4.6.1.a can be expressed in terms of the mass transfer coefficients defined in section 4.6.3.b. The comparison of equations (4.31), (4.32) and (4.44) lead us to

\[ [k^*_0] = \frac{[D_0]}{\ell} [\Phi] \text{exp}[\Phi] - [I]^{-1} \]  

or

\[ [k^*_s] = \frac{[D_s]}{\ell} [\Phi] \text{exp}[\Phi] [[\exp[\Phi] - [I]]^{-1} \]  

where the matrices of zero-flux mass transfer coefficients are given by

\[ [k_0] = [D_0] / \ell \quad \text{and} \quad [k_s] = [D_s] / \ell \]  

and the matrices of correction factors given by

\[ [\Xi_0] = [\Phi] [[\exp[\Phi] - [I]]^{-1} \quad \text{and} \quad [\Xi_s] = [\Phi] [[\exp[\Phi] - [I]]^{-1} \]  

Now equation (4.31) [or (4.32)] is combined with equation (4.40) and with equation (4.56) [or (4.57)] to produce the following equations for the evaluation of the molar fluxes

\[ (N) = c^\nu_j [\beta_0] [k_0] [\Xi_0] (y_0 - y_s) \]  

\[ (N) = c^\nu_j [\beta_s] [k_s] [\Xi_s] (y_0 - y_s) \]  

The matrix of low flux mass transfer coefficients may also be computed in terms of binary mass transfer coefficients using the following expression

\[ [k] = [R]^{-1} \]  

with the elements of matrix [R] defined as:
where the Maxwell-Stefan low flux mass transfer coefficient for the binary pair \(i-j\) is given by

\[
\kappa_{i,j} = \frac{1}{\kappa_{i,i}} \frac{1}{\kappa_{j,j}}
\]

The empirical correlations employed in this work for the evaluation of the Maxwell-Stefan mass transfer coefficients in a binary mixture are presented in Chapter 5.

The same low flux mass transfer coefficients will be used in the evaluation of the matrix \([\Phi]\) necessary in the calculation of the matrices of correction factors. To accomplish this task the following expressions are used:

\[
\Phi_{i,i} = \frac{N_i}{c_i} \frac{N_i}{\kappa_{i,i}} + \sum_{k=1}^{n} \frac{N_k}{c_i} \frac{N_k}{\kappa_{i,k}}
\]

\[
\Phi_{i,j} = -N_i \left( \frac{1}{c_i} \kappa_{i,i} - \frac{1}{c_j} \kappa_{i,j} \right)
\]

It must be clear by now that the amount of computation involved on the evaluation of the fluxes using equations (4.31), (4.32) or (4.60) is not trivial. This is due not only to the matricial operations involved (in particular the exponentiation) but mainly because of the iterative nature of the solution procedure. For the computation of the fluxes one must know the matrix \([\Phi]\) but the knowledge of the fluxes is needed in the evaluation of the matrix \([\Phi]\) [see equations (4.24) and (4.25) or equations (4.65) and (4.66)].

It is well known that irrespective of the iterative scheme adopted its success in
converging towards the solution is strongly influenced by how good the initial guess for the iteration variables was.

In section 4.6.4 some approximate solutions of the Maxwell-Stefan equations are presented. The motivation to do so is twofold:

- they can provide good estimates to be used as starting values for the exact solution iterative procedure;
- they can prove useful in some engineering calculations when one is concerned with the speed and simplicity of the solution procedure but without losing too much accuracy in the results obtained.

### 4.6.4- Some Approximate Solutions of the Maxwell-Stefan Equations

#### 4.6.4.a- The linearised theory of Toor, Stewart, and Prober

The method developed independently by Toor (1964a, b) and by Stewart and Prober (1964) is based on the assumption of a constant matrix of Fickian diffusion coefficients, \([D_{av}]\), along the diffusion path.

Considering steady-state one-dimensional diffusion in an ideal gas mixture a development similar to that presented in sections 4.6.1.a and 4.6.3.d for the exact solution can be devised for this approximate method. In the evaluation of the now constant matrix \([D_{av}]\) some sort of average mole fraction has to be employed. Among others, Smith and Taylor (1983) recommend the usage of the arithmetic average between the mole fractions at the boundaries of the film.

With these considerations in mind, the solution using the linearised theory of Toor-Stewart-Prober can be written as:

\[
(y - y_o) = [\exp[\Psi] - [I]] [\exp[\Psi] - [I]]^{-1} (y_b - y_o) \quad (4.67)
\]

where the elements of the matrix of mass transfer rate factors are calculated from
\[ \Psi_{i,j} = \frac{N_i y_{av_i}}{c_i^V \kappa_{i,nc}} + \sum_{k=1}^{nc} \frac{N_i y_{av_k}}{c_i^V \kappa_{i,k}} \]  \hspace{1cm} (4.68)

\[ \Psi_{i,j} = -N_i y_{av_i} \left( \frac{1}{c_i^V \kappa_{i,j}} - \frac{1}{c_i^V \kappa_{i,nc}} \right) \]  \hspace{1cm} (4.69)

The diffusion fluxes at the boundaries of the film are obtained from

\[ (J_0) = c_i^V [k_0^*] (y_0 - y_{\delta}) \]  \hspace{1cm} (4.70)

\[ (J_{\delta}) = c_i^V [k_{\delta}^*] (y_0 - y_{\delta}) \]

where the matrix of low flux mass transfer coefficients at each boundary of the film are equal and can be calculated from

\[ [k_0] = [k_{\delta}] = [k_{av}] = [R_{av}]^{-1} \]  \hspace{1cm} (4.71)

with the elements of matrix \([R_{av}]\) defined as

\[ R_{av,i,j} = \frac{y_{av_i}}{\kappa_{i,nc}} + \sum_{k=1}^{nc} \frac{y_{av_k}}{\kappa_{i,k}} \]  \hspace{1cm} (4.72)

\[ R_{av,i,j} = -y_{av_i} \left( \frac{1}{\kappa_{i,j}} - \frac{1}{\kappa_{i,nc}} \right) \]  \hspace{1cm} (4.73)

and the finite flux mass transfer coefficients matrix calculated using

\[ [k_{\delta}^*] = [k_{av}] [\Xi_0] \quad \text{or} \quad [k_{\delta}^*] = [k_{av}] [\Xi_{\delta}] \]  \hspace{1cm} (4.74)

with the matrices of correction factors computed from

\[ [\Xi_0] = [\Psi] [\exp[\Psi] - [I]]^{-1} \]  \hspace{1cm} (4.75)

\[ [\Xi_{\delta}] = [\Psi] [\exp[\Psi] [\exp[\Psi] - [I]]^{-1} \]

Now, by invoking the bootstrap matrices the molar fluxes are easily obtained
from either form of equation (4.76)

\[
(N) = c^y_i [\beta_0][k_{av}][\Xi_0](y_0 - y_0) \\
(N) = c^y_i [\beta_0][k_{av}][\Xi_0](y_0 - y_0)
\]  

(4.76)

4.6.4.b- Explicit method of Krishna

Krishna (1979, 1981) presents an explicit method that eliminates the iterative procedure for the evaluation of the fluxes. The starting point for his procedure is equation (4.77) which resulted from the combination of equation (4.4) (written for unidimensional transfer) and equation (4.40).

\[
(N) = -\frac{c^y_i}{\ell} [\beta][B]^{-1} \frac{d(y)}{d\eta}
\]  

(4.77)

By assuming that the matrix \([\beta][B]^{-1}\) is constant over the film, Krishna was able to integrate equation (4.77) to produce linear composition profiles across the film.

\[
\frac{y_i - y_{ib}}{y_{is} - y_{ib}} = \eta
\]  

(4.78)

If the mole fraction gradients calculated by differentiating equation (4.78) are substituted in equation (4.77) we will obtain

\[
(N) = \frac{c^y_i}{\ell} [\beta_{av}][D_{av}](y_0 - y_0) \text{ or } (J) = \frac{c^y_i}{\ell} [D_{av}](y_0 - y_0)
\]  

(4.79)

and considering equation (4.58)

\[
(N) = c^y_i [\beta_{av}][k_{av}](y_0 - y_0) \text{ or } (J) = c^y_i [k_{av}](y_0 - y_0)
\]  

(4.80)

4.6.4.c- Explicit method of Taylor and Smith

Taylor and Smith (1982) generalised the method presented by Burghardt and
Krupiczka (1975) that was originally developed to deal with the diffusion of $m$ components through $nc-m$ stagnant gases. The development of Taylor and Smith's method also starts with equation (4.77) into which they introduced the mole fraction weighted sum of the determinacy coefficients, $\overline{v}$. Therefore the equation to be solved now is

$$\overline{v}(N) = -\frac{c v}{\ell} \overline{v}[\beta][B]^{-1} \frac{d(y)}{dn}$$  \hspace{1cm} (4.81)

with

$$\overline{v} = \sum_{j=1}^{nc} v_j y_j$$ \hspace{1cm} (4.82)

In their analysis they assume that the matrix $\overline{v}[\beta][B]^{-1}$ evaluated at some average composition is constant. Bearing in mind this simplification, the solution of equation (4.81) leads to

$$(N) = \frac{c v}{\ell} \Xi [\beta_{av}][D_{av}](y_0 - y_b) \quad \text{or} \quad (J) = \frac{c v}{\ell} \Xi [D_{av}](y_0 - y_b)$$ \hspace{1cm} (4.83)

that can be written with the aid of equation (4.58) as

$$(N) = c v \Xi [\beta_{av}][k_{av}](y_0 - y_b) \quad \text{or} \quad (J) = c v \Xi [k_{av}](y_0 - y_b)$$ \hspace{1cm} (4.84)

where

$$\Xi = \Phi \left( \frac{\exp \Phi + 1}{\exp \Phi - 1} \right) \quad \text{and} \quad \Phi = \ln \frac{\overline{v}_b}{\overline{v}_0}$$ \hspace{1cm} (4.85)

It is worth emphasising that the only difference between the explicit methods of Krishna and the explicit method of Taylor and Smith lies in the use of the scalar correction factor, $\Xi$, in equations (4.83) and (4.84).

4.6.4.d - Effective diffusivity methods

One of the oldest simplifications introduced when dealing with multicomponent mass transfer is to assume that the rate of diffusion of a component in a
multicomponent mixture depends only on its composition gradient. With this simplification in mind the diffusion fluxes can be computed from

$$J_i = -c_i^y D_{i,\text{eff}} \nabla y_i$$

(4.86)

where $D_{i,\text{eff}}$ is an effective diffusion coefficient of component $i$ in the multicomponent mixture. There are in the literature several proposed relations for the evaluation of the effective diffusion coefficients and we will present below some examples.

Bird et al. (1960) solved equation (4.86) for the mole fraction gradients and equated the result to that obtained using the Maxwell-Stefan equations [equation (4.3)], leading to

$$D_{i,\text{eff}} = \frac{N_i - y_i N_i}{\sum_{j=1}^{nc-1} (y_i D_{i,j})(y_j N_i - y_i N_j)}$$

(4.87)

Stewart (1954) equated equation (4.86) with the generalised Fick's law [equation (4.12)] producing

$$D_{i,\text{eff}} = \sum_{k=1}^{nc-1} D_{i,k} \frac{\nabla y_k}{\nabla y_i}$$

(4.88)

For practical calculations Stewart suggests the substitution of the mole fraction gradients on equation (4.88) by mole fraction differences.

A simplification of equation (4.87) for diffusion of component $i$ through a mixture of stagnant gases was presented by Wilke (1950) as:

$$D_{i,\text{eff}} = \frac{1 - y_i}{\sum_{j=1}^{nc} D_{i,j} y_j}$$

(4.89)

As pointed out by Taylor and Krishna (1993) many authors have been using
Wilke's simplification for the estimation of $D_{i_{\text{eff}}}$ for all components in a mixture even if none of the components has a zero flux.

Considering a constant value of $D_{i_{\text{eff}}}$ calculated at a conveniently averaged composition equation (4.86) can be integrated to produce the composition profiles. With this information at hand the composition gradients can be found and, finally, the diffusion fluxes will be given by

$$J_{i_0} = c_i^V k_{i_{\text{eff}}} \Xi_{i_{\text{eff}}} (y_{i_0} - y_{i_0})$$  \hspace{1cm} (4.90)

where the low flux mass transfer coefficient, $k_{i_{\text{eff}}}$, has been computed using the effective diffusivity of component $i$ and the high flux correction factor is defined via

$$\Xi_{i_{\text{eff}}} = \frac{\Phi_{i_{\text{eff}}}}{\exp \Phi_{i_{\text{eff}}} - 1}$$  \hspace{1cm} (4.91)

and the effective mass transfer rate factor given by

$$\Phi_{i_{\text{eff}}} = \frac{N_i}{c_i^V k_{i_{\text{eff}}}}$$  \hspace{1cm} (4.92)

Smith and Taylor (1983) highlight as one of the major drawbacks of the effective diffusivities methods their failure to account for the interaction effects described in section 4.4. They stress that the formulation presented by Stewart, here represented as equation (4.88), is the best in this aspect.

**4.6.5- Film Model for Nonideal Fluid Systems**

**4.6.5.a- Exact solution**

The starting point for the development of an exact solution is equation (4.93) which resulted from the combination of the Maxwell-Stefan equation for nonideal fluids [equation (4.10)] with equation (4.34) written in $nc-1$ dimensional form.
\[
\frac{d(x - \rho)}{d\eta} = [Y]((x) - (\rho))
\]  

(4.93)

where

\[
[Y] = \frac{N_i\ell}{c_i} [D]^{-1} = \frac{N_i\ell}{c_i} [\Gamma]^{-1}[B] \quad \text{and} \quad \rho = \frac{N_i}{N_t}
\]  

(4.94)

Unlike what would happen for ideal systems, the matrix \([Y]\) is a function of \(\eta\) and therefore equation (4.93) is a first-order matrix differential equation of order \(nc-1\) with a variable coefficient matrix. The solution of this equation following the procedure presented by Amundson (1966) is:

\[
(x - \rho) = \left[\Omega_0(Y)\right](x_0 - \rho)
\]  

(4.95)

where \(\left[\Omega_0(Y)\right]\), the matrizant of \([Y]\) is given by

\[
\left[\Omega_0^l(A)\right] = [I] + \int_0^l [A(t_1)dt_1] + \int_0^l [A(t_1)dt_1]\int_0^l [A(t_2)dt_2] + \int_0^l [A(t_1)dt_1]\int_0^l [A(t_2)dt_2]\int_0^l [A(t_3)dt_3]+ \ldots
\]  

(4.96)

The introduction of the boundary conditions of the film model in equation (4.95) allows us to write the composition profile as

\[
(x - x_0) = \left[\left[\Omega_0(Y)\right] - [I]\right]\left[\left[\Omega_0^l(Y)\right] - [I]\right]^{-1}(x_0 - x_0)
\]  

(4.97)

By differentiation of equation (4.97) the composition gradients are obtained as

\[
\frac{d(x)}{d\eta} = [Y]\left[\left[\Omega_0(Y)\right] - [I]\right]\left[\left[\Omega_0^l(Y)\right] - [I]\right]^{-1}(x_0 - x_0)
\]  

(4.98)

The diffusion fluxes at the boundaries of the film can be obtained by combining equations (4.10) and (4.98) as

\[
(J_0) = \frac{c_i\ell}{\ell} \left[\left[\Gamma_0\right]\right][Y_0]\left[\left[\Omega_0(Y)\right] - [I]\right]^{-1}(x_0 - x_0)
\]  

(4.99)
and considering the definition of the finite flux mass transfer coefficients given in equation (4.44) one arrives at:

\[
\begin{align*}
[k^*_i] &= \frac{[B_0]}{[\Gamma_0]} [Y_0][\Omega^*_0(Y)]^{-1} - [I]^{-1} \\
[k^*_s] &= \frac{[B_s]}{[\Gamma_s]} [Y_s][\Omega^*_s(Y)]^{-1} - [I]^{-1}
\end{align*}
\] (4.102)

As Taylor and Krishna (1993) stressed this solution is extremely cumbersome because of the need to know the composition profiles to evaluate the matrization of \([\mathbf{Y}]\). They recommend the use of one of the approximate methods presented in the following section.

### 4.6.5.b- Approximate solutions

The non-ideal counterpart of equation (4.27) developed previously for ideal mixtures is equation (4.103). The assumption of constant matrices \([\Gamma]\) and \([D]\) along the diffusion path led Krishna (1977) to develop an approximate solution for equation (4.103).

\[
[\Gamma]^d(x) = [\Phi](x) + (\phi)
\] (4.103)

The solution of equation (4.103) parallels the procedure presented in section 4.6.1.a for the solution of equation (4.27). Therefore the diffusion fluxes can be expressed as
\[ (J_0) = \frac{c_i^t [B_0]}{t} \Gamma_{av} [\Theta][\exp[\Theta] - [I]]^{-1}(x_0 - x_s) \] (4.104)

\[ (J_s) = \frac{c_i^t [B_s]}{t} \Gamma_{av} [\Theta]\exp[\Theta][\exp[\Theta] - [I]]^{-1}(x_0 - x_s) \]

where the augmented matrix of rate factors is given by
\[ [\Theta] = [\Gamma_{av}]^{-1}[\Phi] \] (4.105)

with the matrices of low flux mass transfer coefficients defined as
\[ [k_0] = [B_0]^{-1}[\Gamma_{av}] \quad \text{and} \quad [k_s] = [B_s]^{-1}[\Gamma_{av}] \] (4.106)

and with the matrices of high flux correction factors defined as
\[ [\Xi_0] = [\Theta][\exp[\Theta] - [I]]^{-1} \quad \text{and} \quad [\Xi_0] = [\Theta]\exp[\Theta][\exp[\Theta] - [I]]^{-1} \] (4.107)

the molar fluxes can be computed from
\[ (N) = c_i^t [k_0][\Xi_0](x_0 - x_s) \] (4.108)

\[ (N) = c_i^t [k_s][\Xi_s](x_0 - x_s) \]

The extension of the linearized theory of Toor, Stewart, and Prober presented in section 4.6.4.a to deal with nonideal mixtures can be easily accomplished by simply evaluating the matrix of average multicomponent diffusion coefficients with the following expression
\[ [D_{av}] = [B_{av}^{-1}[\Gamma_{av}] \] (4.109)

Therefore the molar fluxes will be computed from
\[ (N) = c_i^t [k_0][\Psi][\exp[\Psi] - [I]]^{-1}(x_0 - x_s) \] (4.110)

\[ = c_i^t [k_s][\Psi]\exp[\Psi][\exp[\Psi] - [I]]^{-1}(x_0 - x_s) \]
with the average matrix of low flux mass transfer coefficients given by

$$[k_{av}] = [R_{av}]^{-1}[\Gamma_{av}]$$  \hspace{1cm} (4.111)$$

where the elements of matrix $[R_{av}]$ are

$$R_{av,ij} = \frac{x_{av,i}}{\kappa_{i,nc}} + \sum_{k=1}^{nc} \frac{x_{av,k}}{\kappa_{i,k}}$$  \hspace{1cm} (4.112)$$

$$R_{av,ij} = -x_{av,i} \left( \frac{1}{\kappa_{i,j}} - \frac{1}{\kappa_{i,nc}} \right)$$  \hspace{1cm} (4.113)$$

and the matrix of mass transfer rate factors is found with the help of the following equations

$$[\Psi] = [\Gamma_{av}]^{-1}[\Psi]$$  \hspace{1cm} (4.114)$$

$$\Psi_{ij} = \frac{N_t x_{av,i}}{c_t^\alpha \kappa_{i,nc}} + \sum_{k=1}^{nc} \frac{N_t x_{av,k}}{c_t^\alpha \kappa_{i,k}}$$  \hspace{1cm} (4.115)$$

$$\Psi_{ij} = -N_t x_{av,i} \left( \frac{1}{c_t^\alpha \kappa_{i,j}} - \frac{1}{c_t^\alpha \kappa_{i,nc}} \right)$$  \hspace{1cm} (4.116)$$

The explicit method of Krishna (section 4.6.4.b) is extended to analyse the mass transfer in nonideal mixtures by considering the constancy of the matrix $[\beta][B]^{-1}[\Gamma]$. The procedure for evaluation of the fluxes is the same leading to the expressions

$$ (N) = \frac{c_t^\alpha}{\ell} [\beta_{av}] [B_{av}]^{-1}[\Gamma_{av}] (x_0 - x_s) \quad \text{or} \quad (J) = \frac{c_t^\alpha}{\ell} [B_{av}]^{-1}[\Gamma_{av}] (x_0 - x_s) $$  \hspace{1cm} (4.117)$$

Taylor (1991) presents an extension of the explicit method of Taylor and Smith (section 4.6.4.c) to encompass nonideal multicomponent mixtures. This time the matrix $\bar{\nu}[\beta][B]^{-1}[\Gamma]$ is considered constant leading to the following expression for the evaluation of the fluxes
\[ (N) = \frac{c_i^l}{\ell} \Xi [B_{av}][B_{av}]^T [\Gamma_{av}] (x_0 - x_8) \]  

(4.118)

where the elements of the matrix \( [\Gamma] \) are defined as

\[ \Gamma_{i,j} = \delta_{i,j} + x_i \left( \frac{\partial \ln \gamma_i}{\partial x_j} \bigg|_{T,P,T} - \frac{\gamma_i}{\nu_n} \frac{\partial \ln \gamma_i}{\partial x_n} \bigg|_{T,P,T} \right) \]  

(4.119)

and

\[ \bar{v} = \sum_{j=1}^{n_c} v_j x_j \]  

(4.120)

The \( \Sigma \) in equation (4.119) indicates that the derivatives must be evaluated keeping constant all the mole fractions except that of component \( j \).

### 4.6.6- Simultaneous Mass and Heat Transfer

In day to day routine chemical engineers almost always have to deal with nonisothermal systems. Therefore, even when one is mainly interested in the mass transfer process it must be analysed in conjunction with the heat transfer process.

As Taylor and Krishna (1993) stressed, the coupling between mass and thermal fluxes is very small in classical unit operations and therefore it is not worth considering the Dufour and Soret effects when analysing operations like conventional distillation.

Similar to the development in section 4.6.3 one could define a heat transfer coefficient as

\[ \dot{q} = \lim_{N_i \to 0} \frac{q}{c_i^v \frac{C_v}{p_m} \Delta T} \]  

(4.121)

Even though with the definition presented in equation (4.121) the analogies
between heat and mass transfer would be more easily noticed, traditionally the zero flux heat transfer coefficient is defined as

\[ h = \lim_{N_i \to 0} \frac{q}{\Delta T} \]  \hspace{1cm} (4.122)

In the same way the composition profiles are distorted by finite mass fluxes the temperature profiles and the heat fluxes will be affected by the presence of finite mass fluxes. With this concern in mind a finite-flux heat transfer coefficient is defined as:

\[ h^* = \frac{q}{\Delta T} \]  \hspace{1cm} (4.123)

One can also introduce a correction factor, \( \Xi_h \), to consider the effect of finite mass fluxes on the zero-flux heat transfer coefficient

\[ h^* = h \Xi_h \]  \hspace{1cm} (4.124)

4.6.6.a- The film model for simultaneous mass and energy transfer

The film model as presented in section 4.6.1 will be extended to analyse the energy transfer across the interface. As assumed in the mass transfer analysis, the resistance to heat transfer is considered as concentrated in a thin film where the transfer occurs by heat conduction. The temperature gradients in the bulk fluid are washed out due to the high degree of mixing outside the film.

The temperature gradients across the film affect the values of physical, thermodynamic, and transport properties. At this stage the property variation will be dealt with by the introduction of average values of the properties. With this simplification the mass transfer analysis presented so far remains unchanged and there is only the need to take into account the effect of mass transfer on the heat transfer process.

For steady-state unidimensional heat transfer across a planar film the energy
Chapter 4 - Multicomponent Mass Transfer

The energy flux, $E$, is constant.

$$\frac{dE}{dz} = 0 \quad \text{or} \quad E = E_0 = E_\delta = \text{constant} \quad (4.125)$$

The conductive contribution for the energy flux is computed using Fourier's law of heat conduction

$$q = -\lambda \nabla T \quad (4.126)$$

and with this contribution, the energy flux is calculated from

$$E = -\lambda \frac{dT}{dz} + \sum_{i=1}^{nc} N_i \overline{H}_i \quad (4.127)$$

Equation (4.127) is subject to the following boundary conditions

$$T\bigg|_{z=z_0} = T_0 \quad (4.128)$$
$$T\bigg|_{z=z_4} = T_\delta \quad (4.128)$$

Considering the reference state for the computation of the partial molar enthalpies to be the pure component at temperature $T_R$ one can write

$$\overline{H}_i = \bar{C}_p i (T - T_R) \quad (4.129)$$

where it was further assumed that the molar heat capacity of component $i$ is not a function of the temperature.

Introducing the dimensionless position, $\eta$, and the heat transfer rate factor, $\Phi_{Ht}$, in equation (4.127) one gets

$$\frac{d(T - T_R)}{d\eta} = \Phi_{Ht} (T - T_R) \frac{E}{\lambda/\ell} \quad (4.130)$$

where
\[
\Phi_H = \sum_{i=1}^{nc} \frac{N_i \mathcal{C}_{pi}}{\lambda_i \ell}
\]

(4.131)

The solution of equation (4.130) for constant values of the thermal conductivities and heat capacities is

\[
\frac{T - T_0}{T_\delta - T_0} = \frac{\exp(\Phi_H \eta) - 1}{\exp(\Phi_H) - 1}
\]

(4.132)

Now the conductive heat flux at \( \eta = 0 \) can be found from

\[
q|_{\eta=0} = -\frac{\lambda}{\ell} \frac{d T}{d \eta}|_{\eta=0}
\]

(4.133)

and with the temperature gradient obtained from equation (4.132) the final expression for the evaluation of the conductive heat flux is

\[
q|_{\eta=0} = h^* (T_0 - T_\delta) = h \Xi_H (T_0 - T_\delta)
\]

(4.134)

with

\[
h = \frac{\lambda}{\ell} \quad \text{and} \quad \Xi_H = \frac{\Phi_H}{\exp \Phi_H - 1}
\]

(4.135)

The heat transfer high flux correction factor \( \Xi_H \) is also known as the Ackermann correction factor.

4.6.6.b- Interphase mass and energy transfer

Let us analyse the simultaneous mass and energy transfer across the phase boundary represented schematically in Figure 4.4.

Considering steady state there must be continuity of the component molar fluxes across the interface. The same applies for the total molar fluxes and to the energy fluxes. Therefore we can write
The fluxes in equation (4.136) result from the diffusive (or conductive) and convective contributions. Using the definitions of mass transfer coefficients [equation (4.44)] and of heat transfer coefficients [equation (4.134)] one can write

\[
\frac{N_i}{V} = C_i^V \left[ k_i^V \right] (y_i - y_i') + N_i (y_i') \tag{4.137}
\]

\[
\frac{N_i}{L} = C_i^L \left[ k_i^L \right] (x_i - x_i') + N_i (x_i') \tag{4.138}
\]

\[
h_i^V (T_i^V - T') - h_i^L (T' - T_i^L) + \sum_{i=1}^{\infty} N_i \left( \overline{H_i^V} - \overline{H_i^L} \right) = 0 \tag{4.139}
\]

As the two phases are assumed to be in equilibrium at the interface the mole fractions at the interface are related by

\[
y_i' = K_i x_i' \tag{4.140}
\]

Equations (4.137) to (4.140) are to be solved together with expressions forcing the summation of the mole fractions at the interface to be equal to unity.
There is a total of $3nc+1$ independent equations in the film model for interphase mass and heat transfer, namely:

- $nc$ rate equations for the vapour phase [equation (4.137)];
- $nc$ rate equations for the liquid phase [equation (4.138)];
- 1 energy balance at the interface [equation (4.139)];
- $nc$ equilibrium equations at the interface [equation (4.140)];
- 2 equations for the mole fraction summation at the interface [equation (4.141)].

The solution of this set of equations will generate the values of the following $3nc+1$ variables:

- $nc$ molar fluxes across the interface;
- the interface temperature;
- $2nc$ mole fractions at the interface.

To completely specify the problem one has to assign values for the remaining variables appearing in equations (4.137) to (4.141). The normal input data are the bulk phase properties (mole fractions and temperature) and the system pressure. Using this data and some appropriate models the necessary thermodynamic, transport, and physical properties are computed.

As Taylor and Krishna (1993) stressed, the interphase energy balance [equation (4.139)] plays the role of the 'bootstrap' equation needed to allow us to compute all the $nc$ molar fluxes.

4.6.7- Which Method to Use?
In this Chapter several different methods to compute the rates of multicomponent mass transfer were presented. With the increasing number of
alternative procedures one needs to know which method is better for the specific problem at hand.

The most comprehensive statistical comparison of some of the approximate solutions of the Maxwell-Stefan equations for a film model of steady state diffusion was presented by Smith and Taylor (1983). They compared the results obtained using the exact solution presented by Krishna and Standart (1976a) [sections 4.6.1.a and 4.6.3.d] with those obtained using the following approximate solutions:

- linearised theory of Toor-Stewart-Prober [section 4.6.4.a];
- explicit method of Krishna [section 4.6.4.b];
- explicit method of Taylor and Smith [section 4.6.4.c];
- effective diffusivity method using Stewart's definition [section 4.6.4.d, equation (4.88)]
- effective diffusivity method using Wilke's definition [section 4.6.4.d, equation (4.89)]
- two other simple effective diffusivity methods.

The general conclusions presented by Smith and Taylor (1983) are:

- the assumption of a constant matrix of multicomponent diffusion coefficients over the diffusion path (linearised theory of Toor-Stewart-Prober) is in general an excellent one; they report the solution of the linearised equations always provided good estimates of the individual fluxes;
- the effective diffusivity methods are lamentably inadequate except when using Stewart's definition;
- if a 'simple' approach is desired one of the explicit methods is recommended; despite some good results when using the effective diffusivity method with Stewart's definition the explicit methods generally give better results and are simpler to use;
- an extremely powerful procedure would be to use the exact solution using initial estimates computed using Taylor and Smith's explicit method.
One can also observe from Taylor and Smith's data that for nonequimolar distillation problems there is little to choose from Taylor and Smith's explicit method, from the linearised theory of Toor-Stewart-Prober, and even from the exact solution. For this reason the linearised theory of Toor-Stewart-Prober has been chosen for the computation of the interphase mass transfer rates in the 'rigorous' reduced-order model to be developed.

As one must be aware, for the rigorous computation of the interphase mass and energy fluxes, it will be necessary the evaluation of several transport, thermodynamic and physicochemical properties of vapour and liquid mixtures. The following Chapter is intended to present the methods employed in this work in the evaluation of such properties.
5- EVALUATION OF TRANSPORT, THERMODYNAMIC, AND PHYSICOCHEMICAL PROPERTIES

5.1- INTRODUCTION

It is well known that one of the key steps in the rigorous simulation of a separation process lies on the evaluation of the necessary thermodynamic, physicochemical, and transport properties.

In this chapter the methods employed throughout this work are described. The major source for property prediction methods is undoubtedly the book of Reid et al. (1987). It must be clear that it is outside the scope of this work to present a complete review on such prediction methods. The aim here is to develop subroutines that are general to some extent and that are capable of providing the desired properties with a good accuracy.

It is also important to stress that for some systems the method employed is not the best possible choice. As our goal is to compare the performance of different models for the separation columns using the same property prediction methods this will not be a cause of major concern.

5.2- DENSITIES

5.2.1- Vapour Phase Density

Following the recommendation of Reid et al. (1987) the Soave-Redlich-Kwong (SRK) equation of state [Soave (1972)] was used in the computation of the vapour phase densities. The SRK equation of state is recommended for nonpolar molecules near saturated conditions. One of the possible formulations of the SRK equation of state is:

\[ z^3 - z^2 + (A - B - \tilde{B} \tilde{z}) z - A\tilde{B} = 0 \]  \hspace{1cm} (5.1)

\[ \tilde{A} = \frac{aP}{R^2 T^2} \quad \text{and} \quad \tilde{B} = \frac{bP}{R T} \]  \hspace{1cm} (5.2)
Chapter 5 - Evaluation of Transport, Thermodynamic, and Physicochemical Properties

\[ a = \frac{0.42748 R^2 T_c^2}{P_c} \left[ 1 + f_o \left( 1 - T_r^2 \right) \right]^2 \]  
(5.3)

\[ b = \frac{0.08664 R T_c}{P_c} \]  
(5.4)

\[ f_o = 0.48 + 1.574 \omega - 0.176 \omega^2 \]  
(5.5)

The mixing rules that allow one to use the SRK equation of state for the evaluation of the vapour density of mixtures are:

\[ a_m = \sum_i \sum_j y_i y_j (a_i a_j)^{1/3} \left( 1 - \overline{k}_{ij} \right) \]  
(5.6)

\[ b_m = \sum_i y_i b_i \]  
(5.7)

For hydrocarbon pairs, \( \overline{k}_{ij} \) is usually taken as zero. If all \( \overline{k}_{ij} \) are zero, equation (5.6) can be rewritten as:

\[ a_m = \left( \sum_i y_i a_i \right)^2 \]  
(5.8)

The largest value of \( z \) that satisfies equation (5.1) is used to evaluate the vapour density according to:

\[ \rho_v = \frac{PM}{zRT} \]  
(5.9)

The subroutine ROENT evaluates the density of the vapour phase, \( \rho_v \), in kg/m\(^3\) and the molar density of the vapour phase, \( \rho_m^v \), in mol/m\(^3\).

### 5.2.2- Liquid Phase Density

The SRK equation of state as described in the previous section is employed in the evaluation of the liquid phase densities. The liquid mole fractions, \( x_i \), replace the vapour mole fractions, \( y_i \), in equations (5.6) to (5.8) and the
smallest value of $z$ that satisfies equation (5.1) is used to evaluate the molar volume according to:

$$\tilde{V}_L = \frac{zRT}{P} \quad (5.10)$$

Following recommendations of Peneloux and Rauzy (1982) the predicted value of the molar volume calculated with equation (5.10) is improved by subtraction of a correction, $c$, calculated with the following equation.

$$c = \sum_{j=1}^{n_c} c_j x_j \quad (5.11)$$

where

$$c_j = 0.40768(0.29441 - z_{RA}) \frac{RT_k}{P_c} \quad (5.12)$$

Some values of the Rackett compressibility factor, $z_{RA}$, can be found on Reid et al. (1987). The liquid density is finally calculated from:

$$\rho_L = \frac{M_m}{\tilde{V}_L - c} \quad (5.13)$$

The subroutine ROENT evaluates the density of the liquid phase, $\rho_L$, in kg/m³ and the molar density of the liquid phase, $c^L$, in mol/m³.

### 5.3- Enthalpies

#### 5.3.1- Vapour phase enthalpy

The vapour-phase enthalpy is calculated as the contribution of two terms. The first term on the right hand side of equation (5.14) is the ideal gas enthalpy, while the second term is the enthalpy departure function for a real gas.

$$H^V = \left[ \sum_{i=1}^{n_c} y_i h^V_i \right] + \left( H^V - H^V \right) \quad (5.14)$$
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The ideal gas enthalpy for component \( i \) is calculated

\[
H_i^V = \int_{T_n}^{T} \bar{C}_p^V \, dT = \int_{T_n}^{T} \left( \bar{C}_{T_i} + \bar{C}_{T_i}^2 + \bar{C}_{T_i}^3 \right) \, dT
\]  

(5.15)

Values of the parameters \( \bar{C}_{T_j} (j = 1, \cdots, 4) \) needed for the computation of the ideal gas heat capacity of component \( i \) can be found in Reid et al. (1987) [Appendix A - Property Data Bank].

The enthalpy departure function, will be evaluated using the Soave-Redlich-Kwong equation of state.

\[
H' - H'' = \frac{1}{b} \ln \frac{z}{z + B} \left[ a - T \frac{\partial a}{\partial T} \right] + RT(z - 1)
\]  

(5.16)

The values of \( a, b, B \) and \( z \) are obtained as described in section 5.2.1 and the derivative of \( a \) with respect to the temperature is given by:

\[
\frac{\partial a}{\partial T} = -\frac{R}{2} \left( \frac{0.42748}{T} \right)^{\frac{v}{2}} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} y_i y_j \left( 1 - \bar{k}_{ij} \right) \left[ f_{\omega_i} \left( \frac{a_i T_{c_i}}{P_{c_i}} \right)^{\frac{v}{2}} \right] + f_{\omega_i} \left( \frac{a_i T_{c_i}}{P_{c_i}} \right)^{\frac{v}{2}}
\]  

(5.17)

For hydrocarbons \( \bar{k}_{ij} \) is usually taken as zero leading to the following expression for the evaluation of the vapour-phase enthalpy departure function of hydrocarbon mixtures:

\[
H' - H'' = \frac{1}{b} \ln \frac{z}{z + B} \left[ a + 0.32691 RT^{\frac{v}{2}} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} y_i y_j \left[ f_{\omega_i} \left( \frac{a_i T_{c_i}}{P_{c_i}} \right)^{\frac{v}{2}} \right] + f_{\omega_i} \left( \frac{a_i T_{c_i}}{P_{c_i}} \right)^{\frac{v}{2}} \right] + RT(z - 1)
\]  

(5.18)

For the evaluation of the vapour phase partial molar enthalpy the starting point will be the general equation for the computation of a partial molar property [Perry et al. (1984)]:

\[
\frac{\partial a}{\partial T} = -\frac{R}{2} \left( \frac{0.42748}{T} \right)^{\frac{v}{2}} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} y_i y_j \left( 1 - \bar{k}_{ij} \right) \left[ f_{\omega_i} \left( \frac{a_i T_{c_i}}{P_{c_i}} \right)^{\frac{v}{2}} \right] + f_{\omega_i} \left( \frac{a_i T_{c_i}}{P_{c_i}} \right)^{\frac{v}{2}}
\]  

(5.17)
where the subscript \( x_T \) indicates that all mole fractions are held constant except \( x_i \) and the particular \( x_k \) of the derivative.

Applying equation (5.19) for the vapour phase partial molar enthalpy one will get:

\[
\overline{H}_i^\nu = H^\nu - \sum_{k=1}^{nc} x_k \left( \frac{\partial H^\nu}{\partial y_k} \right)_{T,P,y_T} \tag{5.20}
\]

The subroutine ROENT evaluates the molar enthalpy of the vapour phase, \( H^\nu \), and the vapour phase partial molar enthalpies, \( \overline{H}_i^\nu \), in J/mol.

### 5.3.2- Liquid phase enthalpy

Reid et al. (1987) pointed out that for the evaluation of the enthalpy departures for liquid mixtures no completely satisfactory recommendation can be made. One alternative that has given good results when dealing with hydrocarbon mixtures not containing hydrogen is to use the Soave modification of the Redlich-Kwong equation of state.

Therefore the procedure for the evaluation of the liquid phase molar enthalpy and the liquid phase partial molar enthalpies will be similar to that presented in section 5.3.1, with the following modifications:

- the liquid mole fractions, \( x_i \), will replace the vapour mole fractions, \( y_i \), on equations (5.14), (5.17), (5.18), and (5.20);
- the values of \( a, b, \hat{B} \) and \( z \) are obtained as described in section 5.2.2;
- the molar enthalpy of the vapour phase, \( H^\nu \), is replaced by the molar enthalpy of the liquid phase, \( H^L \), in equations (5.14), (5.16), (5.18), and (5.20);
• the liquid phase partial molar enthalpy, $\overline{H}_l^L$, replaces the vapour phase partial molar enthalpy, $\overline{H}_v^v$, in equation (5.20).

The subroutine ROENT evaluates the molar enthalpy of the liquid phase, $H^L$, and the liquid phase partial molar enthalpies, $\overline{H}_l^L$, in J/mol.

5.4- SURFACE TENSION
Macleod-Sugden's correlation [Macleod (1923) and Sugden (1924a, b)] was recommended by Reid et al. (1987) to estimate the surface tension of nonaqueous liquid mixtures.

$$\sigma^κ_m = \sum_{j=1}^{nc} \{P_j\} (c_i^x x_j - c_i^v y_j)$$

(5.21)

At low pressure equation (5.21) can be simplified to:

$$\sigma^κ_m = \sum_{j=1}^{nc} \{P_j\} c_i^x x_j$$

(5.22)

The parachors of the components, $\{P_j\}$, can be obtained either from general group contribution methods [e.g. Table 11-3 from Reid et al. (1987)] or from data tabulated in the literature [e.g. Quale (1953)].

The subroutine SURTEN evaluates the surface tension of the liquid mixture, $\sigma_m$, in N/m.

5.5- HEAT CAPACITIES

5.5.1- Vapour phase heat capacity
The heat capacity of a real gas can be obtained from equation (5.23) which is also applicable to gas mixtures.

$$\bar{C}_m^v = \bar{C}_m^{v,v} + \Delta \bar{C}_m^v$$

(5.23)
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The heat capacity of the gas mixture in the ideal gas state, $\bar{C}_{pm}^\circ$, is given by:

$$ \bar{C}_{pm}^\circ = \sum y_i \bar{C}_i^\circ $$

(5.24)

and the ideal gas heat capacity of the pure components can be computed from

$$ \bar{C}_i^\circ = \bar{C}_i + \bar{C}_i T + \bar{C}_i T^2 + \bar{C}_i T^3 $$

(5.25)

Values of the constants $\bar{C}_i$ to $\bar{C}_4$ appearing in equation (5.25) can be found on Reid et al. (1987) [Appendix A - Property Data Bank].

The residual heat capacity, $\Delta \bar{C}_{pm}^\circ$, can be evaluated from a pressure explicit equation of state with the aid of equation (5.26).

$$ \Delta \bar{C}_{pm}^\circ = T \int_0^\vartheta \left( \frac{\partial^2 P}{\partial T^2} \right)_\vartheta d\vartheta - \frac{T (\partial P/\partial T)_\vartheta}{(\partial P/\partial \vartheta)_T} - R $$

(5.26)

Using the Soave-Redlich-Kwong equation of state [Soave (1972)] one will get the following expressions needed in the evaluation of the residual heat capacity:

$$ \left( \frac{\partial P}{\partial T} \right)_\vartheta = \frac{RT}{\bar{V}_V - b_m} + \frac{a_m f_{\omega_m}}{T_c m^2 T_x^2 \left[ 1 + f_{\omega_m} \left( 1 - T_c m^2 \right) \right]^2 \left( \bar{V}_V + b_m \bar{V}_V \right)} $$

(5.27)

$$ \left( \frac{\partial P}{\partial \bar{V}} \right)_T = -\frac{RT}{\bar{V}_V - b_m} + \frac{a_m \left( 2 \bar{V}_V + b_m \right)}{\left( \bar{V}_V + b_m \bar{V}_V \right)^2} $$

(5.28)

$$ \int_0^\vartheta \left( \frac{\partial^2 P}{\partial T^2} \right)_\vartheta d\vartheta = \frac{a_m f_{\omega_m} \ln \left( \frac{\bar{V}_V}{\bar{V}_V + b_m} \right)^{\omega_m+1}}{2 b_m T_c m^2 T_x^2 \left[ 1 + f_{\omega_m} \left( 1 - T_c m^2 \right) \right]^2} $$

(5.29)

The evaluation of $a_m$ and $b_m$ follows the procedure described in section 5.2.1. The definition of $f_{\omega}$ is presented in equation (5.5). The mixing rules for the
computation of the mixture acentric factor and mixture pseudocritical temperature are:

\[
\omega_m = \sum_{j=1}^{nc} y_j \omega_j \quad (5.30)
\]

\[
T_{cm} = \frac{0.42748 R^2 \sum_{i=1}^{nc} y_i T_{ci} / P_{ci}}{0.42748 R^2 \sum_{i=1}^{nc} y_i} \quad (5.31)
\]

As already mentioned in section 5.2.1 for hydrocarbon pairs \( \bar{k}_j \) is usually taken as zero and when all of them are zeroes equation (5.31) simplifies to:

\[
T_{cm} = \frac{\left( \sum_{i=1}^{nc} y_i \bar{a}_i \right)^2}{0.42748 R^2 \sum_{i=1}^{nc} y_i T_{ci} / P_{ci}} \quad (5.32)
\]

where

\[
\bar{a}_i = \frac{0.42748 R^2 T_{ci}^2}{P_{ci}} \left\{ 1 + \frac{f_{wi}}{1 - \left( \frac{T_{cm}}{T_{ci}} \right)^{1/2}} \right\}^2 \quad (5.33)
\]

The vapour phase molar volume is calculated from

\[
\bar{V}_v = \frac{1}{c'_v} \quad (5.34)
\]

The subroutine ROENT calculates the heat capacity of the vapour mixture, \( \bar{C}_p^v \), in J/(mol K).

### 5.5.2- Liquid phase heat capacity

The procedure for the evaluation of the liquid phase heat capacity will be similar to that presented in section 5.5.1, with the following modifications:
• the liquid mole fractions, \( x_n \), will replace the vapour mole fractions, \( y_n \), on equations (5.24), (5.30), (5.31), and (5.32);
• the values of \( a_m \) and \( b_m \) are obtained as described in section 5.2.2;
• the vapour phase heat capacity, \( \bar{C}_{p,m}^V \), is replaced by liquid phase heat capacity, \( \bar{C}_{p,m}^L \), in equation (5.23);
• the residual heat capacity for the liquid phase, \( \Delta \bar{C}_{p,m}^L \), will replace the residual heat capacity for the vapour phase, \( \Delta \bar{C}_{p,m}^V \), in equations (5.23) and (5.26);
• the liquid phase molar volume, \( \bar{V}_L \), computed in section 5.2.2, replaces the vapour phase molar volume, \( \bar{V}_V \), in equations (5.27) to (5.29).

The subroutine ROENT calculates the heat capacity of the liquid mixture, \( \bar{C}_{p,m}^L \), in J/(mol K).

5.6- THERMAL CONDUCTIVITIES

5.6.1- Vapour phase thermal conductivity

For the calculation of the thermal conductivity of a vapour mixture the Mason and Saxena (1958) modification of Wassiljewa’s empirical relation [Wassiljewa (1904)] was employed. This method is recommended by Reid et al. (1987) to compute the thermal conductivity of nonpolar gas mixtures.

\[
\lambda_m^V = \sum_{i=1}^{n_c} \frac{y_i \lambda_i^V}{\sum_{j=1}^{n_c} y_j A_{i,j}}
\]  
(5.35)

where

\[
A_{i,j}^L = 1.0 \quad \text{and} \quad A_{i,j}^V = \left[ \frac{1 + \left( \frac{\lambda_{i,ij}}{\lambda_{tr,ij}} \right)^{1/2} \left( M_i/M_j \right)^{1/4}}{8 \left( 1 + M_i/M_j \right)^{1/2}} \right]^2 
\]  
(5.36)
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\[
\frac{\lambda_{tr}}{\lambda_{tr}} = \frac{\Gamma_i \left[ \exp(0.0464T_i) - \exp(-0.2412T_i) \right]}{\Gamma_i \left[ \exp(0.0464T_i) - \exp(-0.2412T_i) \right]} \quad (5.37)
\]

\[
\Gamma_i = 210 \left( \frac{T_i M_i^3}{P_i^4} \right)^{1/6} \quad (5.38)
\]

The required vapour thermal conductivities of the pure components are obtained using the Ely and Hanley method [Hanley (1976) and Ely and Hanley (1983)] that was recommended by Reid et al. (1987) for nonpolar compounds.

\[
\lambda_i^v = 1944\eta_0 H_i + \frac{n_i^*}{M_i} (1320) \left( C_{p_i} - \frac{5R}{2} \right) \quad (5.39)
\]

\[
\eta_i^* = \eta_0 H_i \frac{M_i}{16.04} \quad (5.40)
\]

\[
\eta_i = 10^{-7} \sum_{n=1}^{9} C_n \left( \frac{T_i}{f_i} \right)^{n-4/3} \quad (5.41)
\]

\[
H_i = \left( \frac{16.04}{M_i} \right)^{1/2} \frac{f_i^{1/2}}{h_i^{1/3}} \quad (5.42)
\]

\[
f_i = \frac{T_i}{190.4} \left[ 1 + (\omega_i - 0.011) \left( 0.56553 - 0.86276 \ln T_i^+ - \frac{0.69852}{T_i^+} \right) \right] \quad (5.43)
\]

\[
h_i = \frac{V_{ci}}{99.2} \left[ 1 + (\omega_i - 0.011) (0.3856 - 1.1617 \ln T_i^+) \right]^{0.288} \frac{z_{ci}}{T_i^+} \quad (5.44)
\]

\[
T_i^+ = T_i \quad \text{if} \quad T_i < 2 \quad \text{or} \quad T_i^+ = 2 \quad \text{if} \quad T_i > 2
\]

**Table 5.1. Coefficients \( C_n \) for the series in equation (5.41)**

<table>
<thead>
<tr>
<th>( C_1 ) = 2.90774 ( \times 10^6 )</th>
<th>( C_2 ) = -3.31287 ( \times 10^6 )</th>
<th>( C_3 ) = 1.60810 ( \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_4 ) = -4.3319 ( \times 10^5 )</td>
<td>( C_5 ) = 7.06248 ( \times 10^4 )</td>
<td>( C_6 ) = -7.11662 ( \times 10^3 )</td>
</tr>
<tr>
<td>( C_7 ) = 4.32517 ( \times 10^2 )</td>
<td>( C_8 ) = -1.44591 ( \times 10^1 )</td>
<td>( C_9 ) = 2.03712 ( \times 10^{-1} )</td>
</tr>
</tbody>
</table>
The subroutine KTERVAP computes the thermal conductivity of a vapour mixture, $\lambda^v_m$, in J/(s.m K).

### 5.6.2 Liquid phase thermal conductivity

For the calculation of the liquid-phase thermal conductivity of a mixture the method of Li (1976) will be used. Li proposed

$$\lambda^L_m = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} \phi_i \phi_j \bar{\lambda}_{i,j}$$  \hspace{1cm} (5.46)

with

$$\bar{\lambda}_{i,j} = 2 \left( \frac{1}{\lambda^L_i} + \frac{1}{\lambda^L_j} \right)^{-1}$$  \hspace{1cm} (5.47)

$$\phi_i = \frac{x_i V_a}{\sum_{j=1}^{n_c} x_j V_c_j}$$  \hspace{1cm} (5.48)

The necessary liquid thermal conductivities of the pure components are computed using the Sato-Riedel method as described by Reid et al. (1987). The final equation of this method is:

$$\lambda^L_i = \frac{(1.11/M_i^{0.5})(3 + 20(1 - T_i)^{2/3})}{3 + 20(1 - T_b)^{2/3}}$$  \hspace{1cm} (5.49)

The subroutine LTHERCORN computes the thermal conductivity of a liquid mixture, $\lambda^L_m$, in J/(s.m K).

### 5.7 Viscosities

The subroutine TRANS is an adaptation of the program VISCOS.FOR distributed by the IVC-SEP, Instituttet for Kemiteknik, Danmarks Tekniske Højskole (Package Version: Sep. 1 - May 90) based on the method of Pedersen et al. (1984) and Pedersen and Fredeslund (1986). This is a corresponding
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states method for the prediction of the viscosity of both gaseous and liquid hydrocarbon fluids.

The viscosity of a hydrocarbon mixture is determined by the following expression:

\[
\eta_m(P, T) = \left( \frac{T_{cm}}{T_{cr}} \right)^{\alpha_m} \left( \frac{P_{cm}}{P_{cr}} \right)^{2/3} \left( \frac{M_m}{M_p} \right)^{\alpha_m} \frac{\alpha_m}{\alpha_R} \left( \int \frac{P_{cm} \alpha_R}{P_{cr} \alpha_m} \right) \left( \frac{T_{cm} \alpha_m}{P_{cr}} \right) \left( \frac{T_{cr}}{T_{cm}} \right)^{1/2} \right) \quad (5.50)
\]

where

\[
T_{cm} = \frac{\sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j \left[ \left( \frac{T_{ci}}{P_{ci}} \right)^{1/3} + \left( \frac{T_{cj}}{P_{cj}} \right)^{1/3} \right]^3 \left( \frac{T_{ci} T_{cj}}{P_{ci} P_{cj}} \right)^{1/2}}{\sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j \left[ \left( \frac{T_{ci}}{P_{ci}} \right)^{1/3} + \left( \frac{T_{cj}}{P_{cj}} \right)^{1/3} \right]^3} \quad (5.51)
\]

\[
P_{cm} = \frac{8 \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j \left[ \left( \frac{T_{ci}}{P_{ci}} \right)^{1/3} + \left( \frac{T_{cj}}{P_{cj}} \right)^{1/3} \right]^3 \left( \frac{T_{ci} T_{cj}}{P_{ci} P_{cj}} \right)^{1/2}}{\left\{ \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j \left[ \left( \frac{T_{ci}}{P_{ci}} \right)^{1/3} + \left( \frac{T_{cj}}{P_{cj}} \right)^{1/3} \right]^3 \right\}^2} \quad (5.52)
\]

\[
M_m = \sum_{i=1}^{nc} x_i M_i + 0.291 \left( \sum_{i=1}^{nc} x_i M_i^2 \right) - \sum_{i=1}^{nc} x_i M_i \quad (5.53)
\]

\[
\alpha_m = 1 + 0.747 \times 10^{-5} P_r \rho_r^{4.265} M_m^{0.8579} \quad (5.54)
\]

\[
\alpha_R = 1 + 0.8374 \times 10^{-4} \rho_r^{4.265} \quad (5.55)
\]

\[
\rho_r = \frac{\rho_R \left( \frac{T_{cm} T_{cr} P_{cm}}{P_{cr} \rho_{cr}} \right)}{P_r} \quad (5.56)
\]

The reference substance indicated by the authors is methane and they used a
correlation given by Hanley et al. (1975) in the evaluation of the properties of methane.

The subroutine TRANS evaluates the viscosities of the liquid phase, \( \eta_L \), and of the vapour phase, \( \eta_V \), in kg/(m.s).

### 5.8- DIFFUSION COEFFICIENTS

#### 5.8.1- Vapour phase diffusion coefficient

Following the recommendation of Reid et al. (1987) the evaluation of the vapour phase binary diffusion coefficients was made using the procedure developed by Fuller and co-workers [Fuller and Giddings (1965), Fuller et al. (1966), and Fuller et al. (1969)].

\[
D_{i,j}^V = \frac{0.001437 T^{1.75}}{PM_{av}^{\frac{1}{2}} \left[ (\Sigma_V)^{\frac{1}{2}} + (\Sigma_V)^{\frac{1}{2}} \right]^2}
\]

\[M_{av} = 2\left[ \left( \frac{1}{M_i} \right) + \left( \frac{1}{M_j} \right) \right]^{-1}\]

The value of \( \Sigma_V \) for component \( i \) is found by summing atomic diffusion volume contributions obtained from Table 5.2.

The subroutine DIFUSI evaluates the binary vapour phase diffusion coefficient, \( D_{i,j}^V \), in m\(^2\)/s.

#### 5.8.2- Liquid phase diffusion coefficient

The determination of the binary liquid diffusion coefficients at infinite dilution was made using the well know and widely used Wilke-Chang correlation [Wilke and Chang (1955)].

\[
D_{i,j}^L = \frac{7.4 \times 10^{-8} (\alpha M_j)^{\frac{1}{2}} T}{\eta_j \gamma_i^{0.6}}
\]

(5.59)
According to Wilke and Chang (1955) the association factor of the solvent, \( \alpha \), should be 2.6 if the solvent is water, 1.9 for methanol, 1.5 for ethanol, and 1.0 if the solvent is unassociated.

The subroutine DIFUSI evaluates the binary liquid diffusion coefficients at infinite dilution, \( D_{ij}^0 \), in \( \text{m}^2/\text{s} \).

### Table 5.2. Atomic diffusion volumes [Reid et al. (1987)]

<table>
<thead>
<tr>
<th>Atomic and structural diffusion volume increments</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>15.90</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>Aromatic ring</td>
<td>-18.30</td>
</tr>
<tr>
<td>Heterocyclic ring</td>
<td>-18.30</td>
</tr>
<tr>
<td>F</td>
<td>14.7</td>
</tr>
<tr>
<td>Cl</td>
<td>21.0</td>
</tr>
<tr>
<td>Br</td>
<td>21.9</td>
</tr>
<tr>
<td>I</td>
<td>29.8</td>
</tr>
<tr>
<td>S</td>
<td>22.9</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>16.20</td>
</tr>
<tr>
<td>Kr</td>
<td>24.50</td>
</tr>
<tr>
<td>Xe</td>
<td>32.70</td>
</tr>
<tr>
<td>H(_2)</td>
<td>6.12</td>
</tr>
<tr>
<td>D(_2)</td>
<td>6.84</td>
</tr>
<tr>
<td>N(_2)</td>
<td>18.50</td>
</tr>
<tr>
<td>O(_2)</td>
<td>16.30</td>
</tr>
<tr>
<td>Air</td>
<td>19.70</td>
</tr>
<tr>
<td>CO</td>
<td>18.0</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>26.9</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>35.9</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>20.7</td>
</tr>
<tr>
<td>H(_2)O</td>
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</tr>
<tr>
<td>SF(_6)</td>
<td>71.3</td>
</tr>
<tr>
<td>Cl(_2)</td>
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</tr>
<tr>
<td>Br(_2)</td>
<td>69.0</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>41.8</td>
</tr>
</tbody>
</table>

5.9- \textbf{Equilibrium Ratios (K values) and Thermodynamic Factors}

The vapour and liquid mole fractions of component \( i \) in a vapour liquid mixture in equilibrium are related by the following expression
\[ y_i = K_j x_i \]  
(5.60)

For subcritical components when the pressure is low or moderate, the equilibrium ratio, \( K_i \), can be calculated with the aid of the following expression:

\[ K_i = \frac{y_i P_i^S}{P} \]  
(5.61)

### 5.9.1 - Vapour Pressure

The vapour pressure of the components will be calculated using a three parameter corresponding state equation (Pitzer's expansion):

\[ \ln P_i^S = f^{(0)}(T_i) + \omega_i f^{(1)}(T_i) \]  
(5.62)

Lee and Kesler (1975) presented the following expressions for the analytical evaluation of the functions \( f^{(0)} \) and \( f^{(1)} \):

\[ f^{(0)}(T_i) = 5.92714 - \frac{6.09648}{T_i} - 12.8862 \ln T_i + 0.169347 T_i^6 \]  
(5.63)

\[ f^{(1)}(T_i) = 15.2518 - \frac{15.6875}{T_i} - 13.4721 \ln T_i + 0.43577 T_i^6 \]  
(5.64)

### 5.9.2 - Activity Coefficient

The activity coefficients are calculated using a library of thermodynamic subroutines distributed by the IVC-SEP, Instituttet for Kemiteknik, Danmarks Tekniske Højskole (Package Version: Sep. 1 - May 90). The original group of three subroutines (MODIN, MODTEM, and MODCAL) was slightly modified and allows one to compute the activity coefficients and the derivatives of the logarithm of the activity coefficient with respect to compositions. Both calculations are made using a modified UNIFAC method described by Larsen \textit{et al.} (1987) and Fredenslund \textit{et al.} (1977).

The expressions for the evaluation of the activity coefficient using the modified UNIFAC method are:
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\[ \ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i' \] (5.65)

\[ \ln \gamma_i^c = \ln \left( w_i / x_i \right) + 1 - \left( w_i / x_i \right) \] (5.66)

\[ w_i = \frac{x_i^{2/3}}{\sum_j x_j^{2/3}} \] (5.67)

\[ \ln \gamma_i' = \sum_k v'_k \left( \ln \Gamma_k - \ln \Gamma_k' \right) \] (5.68)

where \( v'_k \) is the number of groups of type \( k \) in molecule \( i \), \( \Gamma_k \) is the activity coefficient of group \( k \) at mixture composition, and \( \Gamma_k' \) is the activity coefficient of group \( k \) at a group composition corresponding to pure component \( i \). These activity coefficients are computed from:

\[ \ln \Gamma_k = \frac{2}{3} Q_k \left\{ - \left[ \ln \left( \sum_m \theta_m \tau_{mk} \right) \right] + 1 - \sum_l \theta_l \tau_{kl} \right\} \] (5.69)

In the modified UNIFAC method the following definitions apply:

\[ r_i = \sum_k v'_k R_k \] (5.70)

\[ \theta_k = \frac{n_k \frac{2}{3} Q_k}{\sum_m n_m \frac{2}{3} Q_m} \] (5.71)

\[ \tau_{mk} = \exp\left(-a_{mk} / T\right) \] (5.72)

The structural parameters \( R_k, \frac{2}{3} Q_k \) for the functional groups and the temperature dependent group interaction parameters, \( a_{mk} \), can be found in tables presented by Larsen et al. (1987).

As mentioned before this library of thermodynamic subroutines also allows one to compute the unconstrained derivatives of the logarithm of activity coefficients with respect to the compositions \( \partial \ln \gamma_i / \partial x_i \bigg|_{T,P,Z} \). These derivatives will become
necessary in the evaluation of the matrix of thermodynamic factors, \([\Gamma]\), according to the following equations presented by Taylor and Krishna (1993)

\[
\Gamma_{i,j} = \delta_{i,j} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \bigg|_{T,P,T,} \quad \text{for} \quad i, j = 1, 2, \cdots, nc - 1
\]

(5.73)

and

\[
\frac{\partial \ln \gamma_i}{\partial x_j} \bigg|_{T,P,T} = \frac{\partial \ln \gamma_i}{\partial x_j} \bigg|_{T,P,T,} - \frac{\partial \ln \gamma_i}{\partial x_{nc}} \bigg|_{T,P,T}
\]

(5.74)

The subroutine KEQUIL computes the equilibrium ratio (K value) for component \(i, K_i\). The subroutine DERGAMA computes the matrix of thermodynamic factors, \([\Gamma]\).

5.10- MASS AND HEAT TRANSFER COEFFICIENTS

5.10.1- Mass transfer coefficients for randomly packed columns

The computation of the vapour phase and liquid phase binary mass transfer coefficients in randomly packed columns will be made using the well known Onda’s correlations [Onda et al. (1968)].

- for the vapour phase

\[
\kappa_{ij}^V = K_O \left( \frac{G}{a_p \eta_v} \right)^{0.7} \left( \frac{\eta_v}{\rho_v B_{ij}^V} \right)^{\frac{1}{3}} \left( a_p d_p \right)^{-2} a_p B_{ij}^V
\]

(5.75)

where \(K_O\) is 5.23 for ring and saddle packings greater than 12mm (or equal) and \(K_O\) is 2.00 for smaller packings.

- for the liquid phase

\[
\kappa_{ij}^L = 0.0051 \left( \frac{\tilde{L}}{a_w \eta_L} \right)^{2/3} \left( \frac{\eta_L}{\rho_L B_{ij}^L} \right)^{-2/3} \left( a_p d_p \right)^{0.4} \left( \frac{g \eta_L}{\rho_L} \right)^{1/3}
\]

(5.76)
where the wetted surface of the packing, $a_w$, is given by

$$a_w = a_p \left[ 1 - \exp \left( -145 \left( \frac{\bar{L}}{\rho \eta \sigma_m} \right)^{0.1} \left( \frac{a_p L^2}{g \rho \sigma_m} \right)^{0.05} \left( \frac{\bar{L}^2}{a_p \sigma_m \rho L} \right)^{0.2} \left( \frac{\sigma_m}{\sigma_c} \right)^{-0.75} \right) \right]$$

(5.77)

Some values of the critical surface tension of the packing material are presented in Table 5.3.

**Table 5.3. Critical surface tension of packing materials [Perry et al. (1984)]**

<table>
<thead>
<tr>
<th>Packing material</th>
<th>$\sigma_c \times 10^3$, N/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>56</td>
</tr>
<tr>
<td>Ceramic</td>
<td>61</td>
</tr>
<tr>
<td>Glass</td>
<td>73</td>
</tr>
<tr>
<td>Paraffin</td>
<td>20</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>33</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>40</td>
</tr>
<tr>
<td>Steel</td>
<td>75</td>
</tr>
</tbody>
</table>

Bravo and Fair (1982) have proposed an improved correlation for the effective interfacial area for mass transfer to be employed with distillation systems together with Onda's correlations.

$$a_e = 0.498 a_p \left( \frac{\sigma_m^{0.5}}{Z_p^{0.4}} \right) \left[ \left( \frac{\eta \bar{L}}{\rho \sigma_m} \right) \left( \frac{6G}{a_p \eta v} \right) \right]^{0.392}$$

(5.78)

### 5.10.2 - Mass transfer coefficients for structured packings

Following the recommendation of Fair and Bravo (1990), the vapour phase and liquid phase binary mass transfer coefficients for structured packings with the geometry shown in Figure 5.1 will be evaluated from the following equations:

- for the liquid phase

$$\kappa_{i,j}^L = 2 \sqrt{B_{i,j}^L u_{\text{sw}}^L / \pi S}$$

(5.79)
Chapter 5 - Evaluation of Transport, Thermodynamic, and Physicochemical Properties

where

\[ u_{\text{eff}}^L = \frac{3A}{2p_L} \left( \frac{\rho_L^2 g}{3\eta_L A} \right)^{\frac{2}{3}} \]  
(5.80)

\[ \Lambda = \frac{\rho_L u_{\text{eff}}^L}{A_i} \frac{Bh}{4S + B} \]  
(5.81)

\[ u_i^L = L/A_i c_i^L \]  
(5.82)

- for the vapour phase

\[ \kappa_{i,j}^V = 0.0338 \frac{B_{i,j}^V}{d_{eq}} \left[ \frac{d_{eq} \rho_v (u_{\text{eff}}^V + u_{\text{eff}}^i) \gamma^{0.8} \left[ \frac{\eta_v}{\rho_v B_{i,j}^V} \right]^{\frac{3}{2}}}{\eta_v} \right] \]  
(5.83)

where

\[ d_{eq} = Bh \left( \frac{1}{B + 2S} + \frac{1}{2S} \right) \]  
(5.84)

\[ u_{\text{eff}}^V = u_i^V / \epsilon \sin \theta \]  
(5.85)

\[ u_i^V = V/A_i c_i^V \]  
(5.86)

\[ \text{Figure 5.1. Geometric properties of typical structured packings.} \]

(a) Flow channel cross section. (b) Flow channel arrangement [adapted from Fair and Bravo (1990)].
The computation of those mass transfer coefficients is based on the assumption that the surface of the packing is completely wetted. Therefore the effective interfacial area for mass transfer will be equal to the specific surface area of the packing, or, $a_e = a_p$.

### 5.10.3- Heat transfer coefficients

Following Taylor and Krishna (1993) the heat transfer coefficients will be evaluated by making use of the well known Chilton-Colburn analogy

\[
h^V = c_i^V \kappa_{\text{eff}}^V \bar{C}_{p_m}^V \left( \frac{\lambda_m^V}{c_i^V D_{\text{eff}}^V \bar{C}_{p_m}^V} \right)^{2/3} \quad (5.87)
\]

and

\[
h^L = c_i^L \kappa_{\text{eff}}^L \bar{C}_{p_m}^L \left( \frac{\lambda_m^L}{c_i^L D_{\text{eff}}^L \bar{C}_{p_m}^L} \right)^{2/3} \quad (5.88)
\]

In the evaluation of the heat transfer coefficients there is the need of the effective diffusion coefficients and the effective mass transfer coefficients. The computation of these variables depends on the mass transfer model employed in the calculation of the interphase mass transfer rates. Therefore these computational details will be dealt separately when developing the different models.

The subroutine MASSTRAN calculates the vapour phase and liquid phase binary mass transfer coefficients, $\kappa_{i,j}^V$ and $\kappa_{i,j}^L$, in m/s and the effective interfacial area for mass transfer, $a_e$, in m$^2$/m$^3$. It also computes the vapour phase and liquid phase heat transfer coefficients, $h^V$ and $h^L$, in J/(s.m$^2$.K).
6- REDUCED-ORDER MODEL 1 - ROM1

6.1- INTRODUCTION

In the previous chapters a review on the background needed for the development of the reduced-order models based on the orthogonal collocation method was presented. Now, in this chapter and in the two chapters to follow, a thorough description of the four reduced-order models developed in this work will be presented.

The reduced-order model 1, ROM1, is an extension to one of the models originally presented by Srivastava and Joseph (1984). Their models were developed to deal with sections of a packed distillation column without intermediate feeds or sidestreams. The model ROM1 was developed for a distillation column with one intermediate feed, a total condenser, and a partial reboiler [see Figure 6.1] but it can be easily adapted for different configurations. Furthermore, their models were dynamic ones while the model ROM1 is for steady-state simulations.

Figure 6.1. Sketch of the distillation column
6.2- MAJOR ASSUMPTIONS ON THE DEVELOPMENT OF THE MODEL

The major assumptions made in the development of the model ROM1 are:

- negligible pressure drop through the bed;
- the molar latent heats of vaporisation for the components in the system were considered equal so that molar vapour and liquid flowrates are constant in the column;
- liquid and vapour streams were assumed to be at bubble and dew temperatures respectively, so there was no need for enthalpy balances;
- the gas phase overall mass transfer coefficient was used for defining the mass transfer rates. The mass transfer coefficient was taken as being equal for each component present in the system. This assumption together with the second assumption leads the problem to be considered as one of equimolar counter diffusion.

6.3- BASIC EQUATIONS OF THE MODEL

The development of the model starts with the steady-state version of some equations developed by Srivastava and Joseph (1984) and presented in Chapter 3. These equations are:

- the vapour phase component balance [equation (3.45)];

\[
- \frac{\partial}{\partial z} (V_i) - \mathcal{N}_i = 0 \quad (6.1)
\]

\[i = 1, 2, \ldots, nc\]

- the overall component balance [equation (3.44)];

\[
\frac{\partial}{\partial z} (L_i) - \frac{\partial}{\partial z} (V_i) = 0 \quad (6.2)
\]

\[i = 1, 2, \ldots, nc\]

The two previous equations are to be solved together with equation (6.3), the liquid phase bubble point relationship.

\[
1 - \sum_{i=1}^{nc} K_i x_i = 0 \quad (6.3)
\]
Equations (6.1) to (6.3) will be written for the rectification section and for the stripping section of the distillation column. They are to be solved subject to the following boundary conditions:

- at the top of the rectification section

\[ y_{i,TR} - x_{i,TR} = 0 \quad i = 1, 2, \ldots, nc \]  \hspace{1cm} (6.4)

- vapour phase balance around the feed point

\[ V y_{i,BR} - \bar{V} y_{i,TS} - F^{vF} y_{i,F} = 0 \quad i = 1, 2, \ldots, nc \]  \hspace{1cm} (6.5)

- liquid phase balance around the feed point

\[ \bar{L} x_{i,TS} - L x_{i,BR} - F^{LF} x_{i,F} = 0 \quad i = 1, 2, \ldots, nc \]  \hspace{1cm} (6.6)

- bottom of the stripping section

\[ y_{i,BS} - y_{i,B} = 0 \quad i = 1, 2, \ldots, nc \]  \hspace{1cm} (6.7)

The partial reboiler is represented by the component mass balances and the equations describing the equilibrium between the streams leaving the reboiler expressed as follows:

\[ \bar{L} x_{i,BS} - \bar{V} y_{i,B} - (\bar{L} - \bar{V}) x_{i,B} = 0 \quad i = 1, 2, \ldots, nc \]  \hspace{1cm} (6.8)

\[ y_{i,B} - K_{i,B} x_{i,B} = 0 \quad i = 1, 2, \ldots, nc \]  \hspace{1cm} (6.9)

\[ 1 - \sum_{i=1}^{nc} K_{i,B} x_{i,B} = 0 \]  \hspace{1cm} (6.10)

The total interphase mass transfer rates appearing in equation (6.1) are calculated using equation (3.53). It is important to stress that one can only write equation (3.53) for all \( nc \) components if one assumes that the overall mass transfer coefficient is the same for all components.

Introducing the dimensionless variables \( z_R^* \) and \( z_S^* \) defined by

\[ z_R^* = \frac{z_R}{z_R} \quad \text{and} \quad z_S^* = \frac{z_S}{z_S} \]  \hspace{1cm} (6.11)
Chapter 6 - Reduced-Order Model 1 - ROM1

into the model equations and considering the assumptions stated in section 6.2 one arrives to the following set of equations:

- **rectification section**

\[-V \frac{\partial y_i}{\partial z_R} - Z_R N_i = 0 \quad i = 1, 2, \ldots, nc \]  
\[(6.12)\]

\[\frac{L}{Z_R} \frac{\partial x_i}{\partial z_R} - \frac{V}{Z_R} \frac{\partial y_i}{\partial z_R^*} = 0 \quad i = 1, 2, \ldots, nc \]  
\[(6.13)\]

- **stripping section**

\[-\bar{V} \frac{\partial y_i}{\partial z_S} - Z_S N_i = 0 \quad i = 1, 2, \ldots, nc \]  
\[(6.14)\]

\[\frac{L}{Z_S} \frac{\partial x_i}{\partial z_S^*} - \frac{\bar{V}}{Z_S} \frac{\partial y_i}{\partial z_S^*} = 0 \quad i = 1, 2, \ldots, nc \]  
\[(6.15)\]

- **boundary conditions**

\[y_i \big|_{z_R=1} - x_i \big|_{z_R=1} = 0 \quad i = 1, 2, \ldots, nc \]  
\[(6.16)\]

\[\bar{V} y_i \big|_{z_S=0} - \bar{V} y_i \big|_{z_S=1} - F^{VF} y_{i,F} = 0 \quad i = 1, 2, \ldots, nc \]  
\[(6.17)\]

\[\bar{L} x_i \big|_{z_S=1} - \bar{L} x_i \big|_{z_S=0} - F^{LF} x_{i,F} = 0 \quad i = 1, 2, \ldots, nc \]  
\[(6.18)\]

\[y_i \big|_{z_S=0} - y_{i,0} = 0 \quad i = 1, 2, \ldots, nc \]  
\[(6.19)\]

The set of equations formed by equations (6.12)-(6.19), the mass transfer rate expression [equation (3.53)], the bubble point relationship [equation (6.3)], and the partial reboiler equations [equations (6.8)-(6.10)] is the basic set of equations on the model ROM1.

### 6.4- Generation of the Reduced-Order Model - Application of the Orthogonal Collocation Procedure

The reduction of the order of the model is achieved applying the orthogonal collocation procedure on the spatial variables \(\dot{z}_R\) and \(\dot{z}_S\). Considering \(n\) internal collocation points in the stripping section and \(m\) internal collocation points in the rectification section.
points in the rectification section one obtains the following equations for the reduced-order model ROM1:

• rectification section

\[ M_{i,j}^r = -V \sum_{k=1}^{m+2} A_{j,k} y_{i,k} - Z_R \left( K_{OG} a_x \right) \left( y_{i,j} - y_{i,j}^* \right) \left( A_x \right)_R = 0 \]  
\( i = 1,2,\ldots,nc \quad j = 2,3,\ldots,m+2 \)  
\[ M_{i,j}^o = L \sum_{k=1}^{m+2} A_{j,k} x_{i,k} - V \sum_{k=1}^{m+2} A_{j,k} y_{i,k} = 0 \]  
\( i = 1,2,\ldots,nc \quad j = 1,2,\ldots,m+1 \)

\[ B_j = 1 - \sum_{i=1}^{nc} K_{i,j} x_{i,j} = 0 \]  
\( j = 1,2,\ldots,m+2 \)

• stripping section

\[ M_{i,j}^r = -V \sum_{k=2}^{n+2} B_{j,k} y_{i,k} - Z_S \left( K_{OG} a_x \right) \left( y_{i,j} - y_{i,j}^* \right) \left( A_x \right)_S = 0 \]  
\( i = 1,2,\ldots,nc \quad j = 2,3,\ldots,n+2 \)

\[ M_{i,j}^o = L \sum_{k=1}^{n+2} B_{j,k} x_{i,k} - V \sum_{k=1}^{n+2} B_{j,k} y_{i,k} = 0 \]  
\( i = 1,2,\ldots,nc \quad j = 1,2,\ldots,n+1 \)

\[ B_j = 1 - \sum_{i=1}^{nc} K_{i,j} x_{i,j} = 0 \]  
\( j = 1,2,\ldots,n+2 \)

• partial reboiler

\[ M_{i,B}^o = L x_{i,(n)} - V y_{i,B} - \left( L - V \right) x_{i,B} = 0 \]  
\( i = 1,2,\ldots,nc \)

\[ E_{i,B} = y_{i,B} - K_{i,B} x_{i,B} = 0 \]  
\( i = 1,2,\ldots,nc \)

\[ B_B = 1 - \sum_{i=1}^{nc} K_{i,B} x_{i,B} = 0 \]  
\( i = 1,2,\ldots,nc \)
• boundary conditions

\[
y_{i,m+2} - x_{i,m+2} = 0 \quad i = 1,2,\ldots,nc \tag{6.29}
\]

\[
V y_{i,(m)} - \bar{V} y_{i,n+2} - F_{V,F} y_{i,F} = 0 \quad i = 1,2,\ldots,nc \tag{6.30}
\]

\[
L x_{k,n+2} - L x_{i,(m)} - F_{L,F} x_{i,F} = 0 \quad i = 1,2,\ldots,nc \tag{6.31}
\]

\[
y_{i,(n)} - y_{i,B} = 0 \quad i = 1,2,\ldots,nc \tag{6.32}
\]

6.5- NUMERICAL SOLUTION OF THE REDUCED-ORDER MODEL

6.5.1- Variables and equations at the collocation points

There are \(2nc+1\) unknown variables at every collocation point and they are ordered in the vector \((x_i)\) as follows:

\[
(x_i)^T = (y_{i,j}, y_{2,j}, \ldots, y_{nc,j}, x_{1,j}, x_{2,j}, \ldots, x_{nc,j}, T_j) \tag{6.33}
\]

The corresponding \(2nc+1\) equations per collocation point are ordered in the vector \((f_j)\) as follows:

\[
(f_j)^T = (M_{i,j}, M_{2,j}, \ldots, M_{nc,j}, M_{i,1}, M_{2,1}, \ldots, M_{nc,1}, B_j) \tag{6.34}
\]

6.5.2- Variables and equations for the packed column

The model for the entire column, considering \(n\) internal collocation points in the stripping section and \(m\) internal collocation points in the rectification section will have \((2nc+1)(n+m+4)+nc+1\) unknown variables and equations.

The variables will be collected in the vector \((x)\), starting from the reboiler and moving upwards in the column as follows:

\[
(x)^T = (x_{1,B}, x_{2,B}, \ldots, x_{nc,B}, T_B, (x_{1,(n)})^T, (x_{2,(n)})^T, \ldots, (x_{n+2})^T, (x_{1,(m)})^T, (x_{2,(m)})^T, \ldots, (x_{m+2})^T) \tag{6.35}
\]
The ROM1 equations for the whole column are expressed in the general functional form

\[
(f(x))^T = (M_{1B}^o, M_{2B}^o, \ldots, M_{nc,B}^o, B_B, (f_{1(n)})^T, (f_{2(n)})^T, \ldots, (f_{n+2})^T,
\]

\[
((f_{1(m)})^T, (f_{2(m)})^T, \ldots, (f_{m+2})^T) = (0)^T
\]  

(6.36)

It must be clear that for the stripping section of the column

- at collocation point 1 equations (6.23) will be replaced by equations (6.27) combined with equations (6.32);
- at collocation point \( n+2 \) equations (6.24) will be replaced by equations (6.31)

and for the rectification section of the column

- at collocation point 1 equations (6.30) will replace equations (6.20);
- at collocation point \( m+2 \) equations (6.29) will replace equations (6.21).

### 6.5.3- Estimation of the overall mass transfer coefficients

For the evaluation of the total interphase mass transfer rates using equation (3.53) it is necessary to compute the overall mass transfer coefficient at every collocation point. This is achieved by means of the following procedure:

- the effective diffusion coefficients for the liquid phase and for the vapour phase, \( D_{i,\text{eff}}^L \) and \( D_{i,\text{eff}}^V \), are calculated using Bird's formulation [equation (4.87)];
- the effective mass transfer coefficients for the liquid phase and for the vapour phase, \( k_{i,\text{eff}}^L \) and \( k_{i,\text{eff}}^V \), are calculated either using Onda's correlations for random packings [equations (5.75) and (5.76)] or the procedure recommended by Fair and Bravo (1990) for structured packings [equations (5.79) and (5.83)];
- the overall vapour phase mass transfer coefficient for component \( i \) is then calculated with equation (6.37) where the slope of the equilibrium line, \( m_i \), was computed numerically.
an average overall vapour phase mass transfer coefficient is then produced using

\[
K_{oa} = \sum_{i=1}^{nc} y_i K_{oa,i}
\]  

(6.38)

### 6.5.4 Solution of ROM1 equations

The system of algebraic equations represented by equation (6.36) was solved using the subroutine C05NDF from the NAG FORTRAN Workstation Library, produced by The Numerical Algorithm Group Ltd. Subroutine C05NDF is a comprehensive routine to find the solution of a system of nonlinear equations by a modification of the Powell hybrid method [Powell (1970)].

The user has to provide initial values for the unknown variables and, on the basis of these values, the average overall vapour phase mass transfer coefficients at every collocation point are calculated. Whenever possible, the overall mass transfer coefficients are updated based on the solution of equation (6.36) and the convergence on their values is sought.
7- REDUCED-ORDER MODEL 2 - ROM2

7.1- INTRODUCTION
The reduced-order model 2, ROM2, is, to some extent, a combination of the nonequilibrium stage model presented in section 2.3 and the reduced-order model presented by Srivastava and Joseph (1984) [see section 3.3]. The model ROM2 was developed for a distillation column with the configuration presented in section 6.1 and, like the model ROM1, it is devised for steady state simulations.

7.2- MAJOR ASSUMPTIONS ON THE DEVELOPMENT OF THE MODEL
The major assumptions made in the development of the model ROM2 are:
- negligible pressure drop through the bed;
- the vapour-liquid interface was considered as a surface offering no resistance to transport and where equilibrium prevails;
- the interphase mass transfer rates were computed using an effective diffusivity approach based on the definition of Bird et al. (1960) [see section 4.6.4.d].

7.3- BASIC EQUATIONS OF THE MODEL
The mathematical model for the distillation column presented in Figure 6.1 is developed using the two film theory of mass transfer.

Considering the differential volume element presented in Figure 3.2 the following relationships can be written:

7.3.1- Mass balances
- Vapour phase mass balance
  \[ -\frac{\partial V}{\partial z_R} - \sum_{i=1}^{\infty} N_i = 0 \] (7.1)
• Vapour phase component mass balances

\[- \frac{\partial (V y_i)}{\partial z_R} - \mathcal{N}_i = 0 \quad i = 1, 2, \ldots, nc \quad (7.2)\]

• Liquid phase mass balance

\[\frac{\partial L}{\partial z_R} + \sum_{i=1}^{nc} \mathcal{N}_i = 0 \quad (7.3)\]

• Liquid phase component mass balances

\[- \frac{\partial (L x_i)}{\partial z_R} + \mathcal{N}_i = 0 \quad i = 1, 2, \ldots, nc \quad (7.4)\]

It is worth emphasising that on writing the mass balances equation (4.136) was already taken into account. Equation (4.136) was based on the assumption that the interface does not offer resistance to transfer and there is no accumulation of mass or energy at the interface.

7.3.2- Energy balances

• Vapour phase energy balance

\[- \frac{\partial (V H^v)}{\partial z_R} - \sum_{i=1}^{nc} \mathcal{N}_i (H_i^v - q^v) = 0 \quad (7.5)\]

• Interface energy balance

\[q^v - q^L + \sum_{i=1}^{nc} \mathcal{N}_i (H_i^v - H_i^L) = 0 \quad (7.6)\]

• Liquid phase energy balance

\[- \frac{\partial (L H^L)}{\partial z_R} + \sum_{i=1}^{nc} \mathcal{N}_i H_i^L + q^L = 0 \quad (7.7)\]
7.3.3- Interface relationships

- Equilibrium at the interface
  \[ y_i' - K_i x_i' = 0 \quad i = 1, 2, \ldots, nc \] (7.8)

- Mole fraction summations
  \[ 1 - \sum_{i=1}^{nc} y_i' = 0 \] (7.9)
  \[ 1 - \sum_{i=1}^{nc} x_i' = 0 \] (7.10)

7.3.4- The rate equations

- Vapour phase mass transfer rate equations

  With the diffusion fluxes computed with the aid of equation (4.90), the vapour phase mass transfer rate equations can be written as:
  \[ N_i - c_i^v a_e (A_i) k_i^{v, eff} \sum_{k=1}^{nc} N_k = 0 \] (7.11)
  \[ i = 1, 2, \ldots, nc - 1 \]

- Liquid phase mass transfer rate equations

  The procedure presented in section 4.6.4.d for ideal systems has to be extended to deal with nonideal fluid systems. Following the ideas of Lightfoot and Scattergood (1965) one can extend the definition of the effective diffusivity presented by Bird et al. (1960). The combination of these ideas allows one to write the liquid phase mass transfer rate equations as:
  \[ N_i - c_i^l a_e (A_i) k_i^{l, eff} \sum_{j=1}^{nc-1} \Gamma_{i,j} (x_j' - x_j') - \bar{x}_i \sum_{k=1}^{nc} N_k = 0 \] (7.12)
  \[ i = 1, 2, \ldots, nc - 1 \]

  The values of the effective mass transfer coefficients, \( k_i^{v, eff} \) and \( k_i^{l, eff} \), are obtained using either equations (5.75) and (5.76) or equations (5.79) and
(5.83) with the effective diffusion coefficients, $D_{i,\text{eff}}^V$ and $D_{i,\text{eff}}^L$, replacing the Maxwell-Stefan diffusivities. The effective diffusion coefficients are computed using equation (4.87)

- Energy transfer rate equation
The conductive heat transfer rates will be computed using equation (4.134) that will lead to:

$$q^V - h^V \Xi H^V a_0 (T^V - T') (A_i) = 0$$  \hspace{1cm} (7.13)

$$q^L - h^L \Xi H^L a_0 (T^L - T') (A_i) = 0$$  \hspace{1cm} (7.14)

In the computation of the heat transfer coefficients, the mixture effective diffusivities, $D_{\text{eff}}^V$ and $D_{\text{eff}}^L$, and the mixture effective mass transfer coefficients, $k_{\text{eff}}^V$ and $k_{\text{eff}}^L$, are calculated using the following formulas:

$$\Pi_{\text{eff}}^V = \frac{\sum_{i=1}^{n_c} y_i \Pi_{i,\text{eff}}^V}{1 - y_{nc}} \quad \text{and} \quad \Pi_{\text{eff}}^L = \frac{\sum_{i=1}^{n_c} x_i \Pi_{i,\text{eff}}^L}{1 - x_{nc}}$$  \hspace{1cm} (7.15)

The heat transfer rate factors necessary to the evaluation of the heat transfer high flux correction factors, $\Xi_H^V$ and $\Xi_H^L$, are computed with the aid of:

$$\Phi_H^V = \frac{\bar{C}_p^V \sum_{i=1}^{n_c} N_i}{h^V} \quad \text{and} \quad \Phi_H^L = \frac{\bar{C}_p^L \sum_{i=1}^{n_c} N_i}{h^L}$$  \hspace{1cm} (7.16)

All the properties used in the evaluation of the interphase mass and heat transfer rates were calculated at the average mole fractions defined by:

$$y_{av} = \frac{y_j + y_j'}{2} \quad \text{and} \quad x_{av} = \frac{x_j' + x_j}{2}$$  \hspace{1cm} (7.17)

7.3.5- Boundary conditions
Equations (7.1) to (7.14) will be written for the rectification section and for the
stripping section of the distillation column. They are to be solved subject to the following boundary conditions:

- at the top of the rectification section

\[
(T_{TR}^L)_{Bub} - T_{TR}^L - T_{SC} = 0 \quad (7.18)
\]

\[
R_R - L_{TR} / (V_{TR} - L_{TR}) = 0 \quad (7.19)
\]

\[
y_{i,TR} - x_{i,TR} = 0 \quad i = 1, 2, \ldots, nc \quad (7.20)
\]

- vapour phase balances around the feed point

\[
V_{BR} - V_{TS} - F^V = 0 \quad (7.21)
\]

\[
V_{BR} y_{i,BR} - V_{TS} y_{i,TS} - F^V y_{i,F} = 0 \quad i = 1, 2, \ldots, nc \quad (7.22)
\]

\[
V_{BR} H_{BR}^V - V_{TS} H_{TS}^V - F^V H^V = 0 \quad (7.23)
\]

- liquid phase balances around the feed point

\[
L_{TS} - L_{BR} - F^L = 0 \quad (7.24)
\]

\[
L_{TS} x_{i,TS} - L_{BR} x_{i,BR} - F^L x_{i,F} = 0 \quad i = 1, 2, \ldots, nc \quad (7.25)
\]

\[
L_{TS} H_{TS}^L - L_{BR} H_{BR}^L - F^L H^L = 0 \quad (7.26)
\]

- bottom of the stripping section plus the partial reboiler

\[
y_{i,BS} - K_{i,B} x_{i,B} = 0 \quad i = 1, 2, \ldots, nc \quad (7.27)
\]

\[
L_{BS} - V_{BS} - B = 0 \quad (7.28)
\]

\[
L_{BS} x_{i,BS} - V_{BS} y_{i,BS} - B x_{i,B} = 0 \quad i = 1, 2, \ldots, nc \quad (7.29)
\]

\[
1 - \sum_{i=1}^{nc} x_{i,B} = 0 \quad (7.30)
\]

Introducing the dimensionless variables \(z_r^*\) and \(z_s^*\) defined by equation (6.11) into the model equations one arrives to the following set of equations:
Chapter 7 - Reduced-Order Model 2 - ROM2

- rectification section

\[ -\frac{\partial V}{\partial z_R^*} - Z_R \sum_{i=1}^{nc} N_i = 0 \]  
(7.31)

\[ -\frac{\partial (V y_i)}{\partial z_R^*} - Z_R N_i = 0 \quad i = 1,2,\ldots, nc \]  
(7.32)

\[ \frac{\partial L}{\partial z_R^*} + Z_R \sum_{i=1}^{nc} N_i = 0 \]  
(7.33)

\[ -\frac{\partial (L x_i)}{\partial z_R^*} - Z_R N_i = 0 \quad i = 1,2,\ldots, nc \]  
(7.34)

\[ -\frac{\partial (V H^v)}{\partial z_R^*} - Z_R \sum_{i=1}^{nc} N_i H_i^v - Z_R q^v = 0 \]  
(7.35)

\[ \frac{\partial (L H^l)}{\partial z_R^*} + Z_R \sum_{i=1}^{nc} N_i H_i^l + Z_R q^l = 0 \]  
(7.36)

- stripping section

\[ -\frac{\partial V}{\partial z_S^*} - Z_S \sum_{i=1}^{nc} N_i = 0 \]  
(7.37)

\[ -\frac{\partial (V y_i)}{\partial z_S^*} - Z_S N_i = 0 \quad i = 1,2,\ldots, nc \]  
(7.38)

\[ \frac{\partial L}{\partial z_R^*} + Z_S \sum_{i=1}^{nc} N_i = 0 \]  
(7.39)

\[ -\frac{\partial (L x_i)}{\partial z_S^*} - Z_S N_i = 0 \quad i = 1,2,\ldots, nc \]  
(7.40)

\[ -\frac{\partial (V H^v)}{\partial z_S^*} - Z_S \sum_{i=1}^{nc} N_i H_i^v - Z_S q^v = 0 \]  
(7.41)

\[ \frac{\partial (L H^l)}{\partial z_S^*} + Z_S \sum_{i=1}^{nc} N_i H_i^l + Z_S q^l = 0 \]  
(7.42)
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- boundary conditions

\[
\left. T^L \right|_{z_R = 1} - T^L \left|_{z_S = 1} - T_{SC} = 0 \right. \\
(7.43)
\]

\[
R_R - L \left|_{z_R = 1} \right) \left( V \right|_{z_R = 1} - L \left|_{z_S = 1} \right) = 0 \\
(7.44)
\]

\[
y_i \big|_{z_R = 1} - x_i \big|_{z_S = 1} = 0 \quad i = 1, 2, \ldots, nc \\
(7.45)
\]

\[
V \big|_{z_S = 0} - V \big|_{z_R = 1} - F_{VF} = 0 \\
(7.46)
\]

\[
(Vy_i) \big|_{z_S = 0} - (Vy_i) \big|_{z_R = 1} - F_{VF} y_{i,F} = 0 \quad i = 1, 2, \ldots, nc \\
(7.47)
\]

\[
(VH^V) \big|_{z_S = 0} - (VH^V) \big|_{z_R = 1} - F_{VF} H^V = 0 \\
(7.48)
\]

\[
L \big|_{z_R = 1} - L \big|_{z_S = 0} - F_{LF} = 0 \\
(7.49)
\]

\[
(Lx_i) \big|_{z_S = 0} - (Lx_i) \big|_{z_R = 1} - F_{LF} x_{i,F} = 0 \quad i = 1, 2, \ldots, nc \\
(7.50)
\]

\[
(LH^L) \big|_{z_R = 1} - (LH^L) \big|_{z_S = 0} - F_{LF} H^L = 0 \\
(7.51)
\]

\[
y_i \big|_{z_S = 0} - K_{i,B} x_{i,B} = 0 \quad i = 1, 2, \ldots, nc \\
(7.52)
\]

\[
L \big|_{z_S = 0} - V \big|_{z_R = 0} - B = 0 \\
(7.53)
\]

\[
(Lx_i) \big|_{z_S = 0} - (Vy_i) \big|_{z_S = 0} - B x_{i,B} = 0 \quad i = 1, 2, \ldots, nc \\
(7.54)
\]

The set of equations formed by equations (7.30)-(7.54), the interface energy balance [equation (7.6)], the interface relationships [equations (7.8)-(7.10)], and the rate equations [equations (7.11)-(7.14)] is the basic set of equations for the model ROM2.

7.4- Generation of the Reduced-Order Model - Application of the Orthogonal Collocation Procedure

The reduction of the order of the model is achieved applying the orthogonal collocation procedure on the spatial variables \( z_R \) and \( z_S \). Considering \( n \)
internal collocation points in the stripping section and $m$ internal collocation points in the rectification section one obtains the following equations for the reduced-order model ROM2:

- **rectification section**

\[
M_j^y = -\sum_{k=1}^{m+2} A_{j,k} V_k - Z_R \sum_{i=1}^{nc} N_{i,j} = 0 \quad (7.55)
\]

\[
M_{i,j}^y = -\sum_{k=1}^{m+2} A_{j,k} V_k y_{i,k} - Z_R N_{i,j} = 0 \quad (7.56)
\]

\[
M_j^l = \sum_{k=1}^{m+2} A_{j,k} L_k + Z_R \sum_{i=1}^{nc} N_{i,j} = 0 \quad (7.57)
\]

\[
M_{i,j}^l = \sum_{k=1}^{m+2} A_{j,k} L_k x_{i,k} + Z_R N_{i,j} = 0 \quad (7.58)
\]

\[
E_j^y = -\sum_{k=1}^{m+2} A_{j,k} V_k H_k^y - Z_R \sum_{i=1}^{nc} N_{i,j} \bar{H}_{i,j}^y - Z_R h_j^y \Xi_{H_j} a_{ij} (T_j^y - T_j^l) (A_{ij})_R = 0 \quad (7.59)
\]

\[
E_j^l = \sum_{k=1}^{m+2} A_{j,k} L_k H_k^l + Z_R \sum_{i=1}^{nc} N_{i,j} \bar{H}_{i,j}^l + Z_R h_j^l \Xi_{H_j} a_{ij} (T_j'^l - T_j^l) (A_{ij})_R = 0 \quad (7.60)
\]

\[
E_j = h_j^y \Xi_{H_j} a_{ij} (T_j^y - T_j^l) (A_{ij})_R - h_j^l \Xi_{H_j} a_{ij} (T_j'^l - T_j^l) (A_{ij})_R + \sum_{i=1}^{nc} N_{i,j} \bar{H}_{i,j}^l = 0 \quad (7.61)
\]

\[
Q_{i,j}^l = y_{i,j}' - K_{i,j} x_{i,j} = 0 \quad (7.62)
\]
The equations for the stripping section are similar to those for the rectification section [equations (7.55)-(7.66)] with the following modifications:

\( i. \) the index \( n \) replaces the index \( m \);

\( ii. \) the orthogonal collocation coefficients \( B_{j,k} \) (for \( n \) internal collocation points) replace the coefficients \( A_{j,k} \) (for \( m \) internal collocation points);

\( iii. \) the height of packing in the stripping section, \( Z_s \), replaces the height of packing in the rectification section, \( Z_r \);

\( iv. \) the cross sectional area of the column on the stripping section, \( (A)_{S} \), replaces the cross sectional area of the column on the enriching section, \( (A)_{R} \).

\[ \text{boundary conditions} \]

\[ (T^L_{m+2})_{Bu} - T^L_{m+2} - T_{SC} = 0 \]  \hfill (7.67)

\[ R_R - L_{m+2}/(V_{m+2} - L_{m+2}) = 0 \]  \hfill (7.68)

\[ y_{i,m+2} - x_{i,m+2} = 0 \quad i = 1,2,\ldots, nc \]  \hfill (7.69)
Chapter 7 - Reduced-Order Model 2 - ROM2

7.5 - Numerical Solution of the Reduced-Order Model

7.5.1 - Variables and equations at the collocation points

There are 5nc+5 unknown variables at every collocation point and they are ordered in the vector \( (x_j) \) as follows:

\[
(x_j)^T = (V_{i,k(n)}, y_{i,k(n)}, y_{2,j}, \ldots, y_{nc,j}, T_j^V, y_{i,j}^V, y_{2,j}^V, \ldots, y_{nc,j}^V, x_{i,j}^L, x_{2,j}^L, \ldots)
\]

(7.80)

The corresponding 5nc+5 equations per collocation point are ordered in the vector \( (f_j) \) as follows:

\[
(f_j)^T = (M_j^V, M_{i,j}^V, M_{2,j}^V, \ldots, M_{nc,j}^V, E_j^V, R_{i,j}^V, R_{2,j}^V, \ldots, R_{nc-1,j}^V, S_j^V, Q_{i,j}^V, Q_{2,j}^V, \ldots)
\]

\[
Q_{nc,j}^V, E_j^L, M_{i,j}^L, M_{2,j}^L, \ldots, M_{nc,j}^L, E_j^L, R_{i,j}^L, R_{2,j}^L, \ldots, R_{nc-1,j}^L, S_j^L\)
\]

(7.81)
7.5.2- Variables and equations for the packed column

The model for the entire column, considering \( n \) internal collocation points in the stripping section and \( m \) internal collocation points in the rectification section will have \((5nc+5)(n+m+4)+nc\) unknown variables and equations.

The variables will be collected in the vector \((x)\), starting from the reboiler and moving upwards in the column as follows:

\[
(x)^T = (x_{1,B}, x_{2,B}, \ldots, x_{nc,B}, (x_{\gamma(n)})^T, (x_{2(n)})^T, \ldots, (x_{n+2})^T, (x_{\gamma(m)})^T, (x_{2(m)})^T, \ldots, (x_{m+2})^T)
\]  \hspace{1cm} (7.82)

The ROM2 equations for the whole column are expressed in the general functional form

\[
(f(x))^T = (Q_{1,B}, Q_{2,B}, \ldots, Q_{nc,B}, (f_{\gamma(n)})^T, (f_{2(n)})^T, \ldots, (f_{n+2})^T, (f_{\gamma(m)})^T, (f_{2(m)})^T, \ldots, (f_{m+2})^T) = (0)^T
\]  \hspace{1cm} (7.83)

It must be clear that for the stripping section of the column

- at collocation point 1 equations (7.55), (7.56), and (7.59) will be replaced by equations (7.77)-(7.79);
- at collocation point \( n+2 \) equations (7.57), (7.58), and (7.60) will be replaced by equations (7.73)-(7.75);

and for the rectification section of the column

- at collocation point 1 equations (7.55), (7.56), and (7.59) will be replaced by equations (7.70)-(7.72);
- at collocation point \( m+2 \) equations (7.57), (7.58), and (7.60) will be replaced by equations (7.67)-(7.69).

7.5.3- Solution of ROM2 equations

The system of algebraic equations represented by equation (7.83) was solved using the subroutine C05NDF already quoted in section 6.5.4.
8- REDUCED-ORDER MODELS 3 AND 4 - ROM3 & ROM4

8.1- INTRODUCTION

The reduced-order models 3 and 4 (ROM3 and ROM4) are improvements on the reduced-order model 2 (ROM2) presented in the previous chapter. These improvements are achieved by the utilisation of a more rigorous procedure in the evaluation of the interphase mass transfer rates. In both models the fluxes were computed using the linearised theory of Toor-Stewart-Prober [see sections 4.6.4.a and 4.6.5.b]. The models ROM3 and ROM4 were developed for a distillation column with the configuration presented in section 6.1 and, like the models ROM1 and ROM2, they are devised for steady state simulations.

8.2- MAJOR ASSUMPTIONS ON THE DEVELOPMENT OF THE MODEL

8.2.1- Model ROM3

The major assumptions made in the development of the model ROM3 are the same presented for model ROM2 with the exception that:

- the interphase mass transfer rates were computed using the linearised theory of Toor-Stewart-Prober [see section 4.6.4.a and 4.6.5.b] but considering the matrices of high flux correction factors, $[\Xi^V_0]$ and $[\Xi^L_0]$, equal to the identity matrix;
- the interphase heat transfer rates were computed using the procedure presented in section 7.3.4 but considering the heat transfer high flux correction factors, $\Xi^V_H$ and $\Xi^V_L$, equal to unity.

8.2.2- Model ROM4

The major assumptions made in the development of the model ROM4 are the same presented for model ROM3 except that now the high flux correction of the mass transfer and heat transfer coefficients are taken into account.
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8.3- BASIC EQUATIONS OF THE MODEL

The basic equations of the models ROM3 and ROM4 are the same presented in section 7.3 for the model ROM2. The only differences are in the rate equations, therefore only those will be presented in this section.

8.3.1- The rate equations for model ROM3

The reader is reminded that on writing the equations on this section use was made of equation (4.136) and the high flux correction factors were not taken into account.

- Vapour phase mass transfer rate equations

The diffusion fluxes in the vapour phase are computed using the linearised theory of Toor-Stewart-Prober [equation (4.70)]. Therefore, combining equations (4.70) and (4.137), the vapour phase mass transfer rate equations can be written as:

\[
(N) - c_i^V [k_{av}^V] a_e ((y) - (y')) A_i - N_i (y) = 0
\]

Substituting equation (4.71) into equation (8.1) and after rearrangement one obtains:

\[
[R_{av}^V(N) - N_i(y)] - c_i^V a_e ((y) - (y')) A_i = 0
\]

with the elements of matrix \([R_{av}^V]\) calculated using equations (4.72) and (4.73).

- Liquid phase mass transfer rate equations

As it happened for the vapour phase, the liquid phase rate equations will be obtained using equation (4.70), but this time it will be combined with equation (4.138) leading to:

\[
(N) - c_i^L [k_{av}^L] a_e ((x') - (x)) A_i - N_i (x) = 0
\]

Substituting equation (4.111) into equation (8.3) and after rearrangement one
obtains:

\[
\begin{bmatrix} R_{av}^L \end{bmatrix} (N) - N_i(x) - c_i \Gamma_{av}^T a_i \left( (x') - (x) \right) (A_i) = (0) \quad (8.4)
\]

with the elements of matrix \([R_{av}^L]\) calculated using equations (4.112) and (4.113).

- Energy transfer rate equation

The conductive heat transfer rates will be computed using equation (4.134) with the Ackermann correction factor taken as equal to unity. This will lead to:

\[
q^V - h^V a_e (T^V - T') (A_i) = 0 \quad (8.5)
\]

\[
q^L - h^L a_e (T' - T^L) (A_i) = 0 \quad (8.6)
\]

The heat transfer coefficients were computed using equations (5.87) and (5.88). The mixture effective diffusivities, \(D_{eff}^V\) and \(D_{eff}^L\), to be used in this computation were found using the following expressions,

\[
D_{eff}^L = \sum_{i=1}^{nc} x_{i,v} \frac{\sum_{k=1}^{nc} D_{i,k}^L}{nc - 1} \quad \text{and} \quad D_{eff}^V = \sum_{i=1}^{nc} y_{i,v} \frac{\sum_{k=1}^{nc} D_{i,k}^V}{nc - 1} \quad (8.7)
\]

while the mixture effective mass transfer coefficients, \(k_{eff}^V\) and \(k_{eff}^L\), were calculated using procedure suggested by Wang and Cameron (1991), represented by the following formulas:

\[
k_{eff}^L = \sum_{i=1}^{nc} x_{i,av} \frac{1 - x_{av_i}}{\sum_{k=1}^{nc} k_{i,k}} \quad \text{and} \quad k_{eff}^V = \sum_{i=1}^{nc} y_{i,av} \frac{1 - y_{av_i}}{\sum_{k=1}^{nc} k_{i,k}} \quad (8.8)
\]

In the evaluation of the averaged matrices, \([R_{av}^V]\), \([R_{av}^L]\), and \([\Gamma_{av}\)], the average mole fractions defined by equations (7.17) were employed.
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The set of equations formed by equations (7.30)-(7.54), the interface energy balance [equation (7.6)], the interface relationships [equations (7.8)-(7.10)], and the rate equations [equations (8.2), (8.4)-(8.6)] is the basic set of equations on the model ROM3.

8.3.2- The rate equations for model ROM4

As in the development of the rate equations for the model ROM3, equation (4.136) will be taken into account when writing the rate equations for the model ROM4.

- Vapour phase mass transfer rate equations

The diffusion fluxes in the vapour phase are computed using the linearised theory of Toor-Stewart-Prober [equation (4.70)]. Therefore, combining equations (4.70) and (4.137), the vapour phase mass transfer rate equations can be written as:

\[ (N) - c_r \left[ k_{av} \Xi_0 \right] a_e (y) - (y') (A_i) - N_i (y) = 0 \]  \hspace{1cm} (8.9)

Substituting equation (4.71) into equation (8.9) and after rearrangement one obtains:

\[ \left[ R_{av} \Xi_0 \right] (N) - N_i (y) - c_r \Xi_0 a_e (y) - (y') (A_i) = 0 \]  \hspace{1cm} (8.10)

with the elements of matrix \( [R_{av}] \) calculated using equations (4.72) and (4.73).

The computation of the matrix of high flux correction factors, \( [\Xi_0] \), was made using Sylvester's expansion formula [equation (8.11)] as presented by Taylor and Krishna (1993).

\[ [\Xi_0] = \sum_{j=1}^{nd} \hat{\Xi}_0 \left\{ \prod_{j=1}^{nd} \left[ [\Psi] - \hat{\Psi}_j \right] \right\} \left\{ \prod_{j=1}^{nd} \left( \hat{\Psi}_i - \hat{\Psi}_j \right) \right\} \]  \hspace{1cm} (8.11)
where \( nd \) is the number of distinct eigenvalues of the matrix of mass transfer rate factors, \( [\Psi] \), and noting that \( nd \leq nc - 2 \). The eigenvalue functions, \( \hat{\Xi}_0 \), are given by:

\[
\hat{\Xi}_0 = \frac{\Psi_i}{\exp \Psi_i - 1}
\]  

(8.12)

The matrix of mass transfer rate factors, \( [\Psi] \), is obtained from equations (4.68) and (4.69).

The eigenvalues of the matrix of transfer rate factors are found using the subroutine F02AFF from the NAG FORTRAN Workstation Library, produced by The Numerical Algorithm Group Ltd.

- Liquid phase mass transfer rate equations
As it happened for the vapour phase, the liquid phase rate equations will be obtained using equation (4.70), but this time it will be combined with equation (4.138) leading to:

\[
(N) - c_i^L \left[ k_{av}^L \Xi_0^L \right] a_s ((x') - (x))(A_t) - N_i(x) = 0
\]  

(8.13)

Substituting equation (4.111) into equation (8.13) and after rearrangement one obtains:

\[
\left[ R_{av}^L \right] ((N) - N_i(x)) - c_i^L \left[ \Gamma_{av}^L \Xi_0^L \right] a_s ((x') - (x))(A_t) = 0
\]  

(8.14)

with the elements of matrix \( R_{av}^L \) calculated using equations (4.112) and (4.113).

The computation of the matrix of high flux correction factors, \( [\Xi_0^L] \), was also made using equation (8.11) but this time the matrix of mass transfer rate factors, \( [\Psi] \), was obtained from equations (4.114), (4.115), and (4.116).
The conductive heat transfer rates were computed using equation (4.134) leading to:

\[
q^V - h^V \Xi^V_{\mu} a_e (T^V - T^I) (A_r) = 0 \quad (8.15)
\]

\[
q^L - h^L \Xi^L_{\mu} a_e (T^I - T^L) (A_r) = 0 \quad (8.16)
\]

The heat transfer coefficients, \( h^V \) and \( h^L \), were computed using equations (5.87) and (5.88) with the mixture effective diffusivities, \( D_{eff}^V \) and \( D_{eff}^L \), calculated with equation (8.7), and with the mixture effective mass transfer coefficients, \( k_{eff}^V \) and \( k_{eff}^L \), calculated using equation (8.8).

The heat transfer high flux correction factors, \( \Xi^V_{H} \) and \( \Xi^L_{H} \), were calculated using equation (4.135) with the heat transfer rate factors, \( \Phi^V_{H} \) and \( \Phi^L_{H} \), computed with equation (7.16).

In the evaluation of the averaged matrices, \([R^V_{av}], [R^L_{av}], [\Psi], \) and \([\Gamma_{av}], \) the average mole fractions defined by equations (7.17) were employed.

The set of equations formed by equations (7.30)-(7.54), the interface energy balance [equation (7.6)], the interface relationships [equations (7.8)-(7.10)], and the rate equations [equations (8.10), (8.14)-(8.16)] is the basic set of equations on the model ROM4.

8.4- Generation of the Reduced-Order Model - Application of the Orthogonal Collocation Procedure

In this section there will be presented only the rate equations and the energy balance functions for the models ROM3 and ROM4 as the remaining equations are the same presented on section 7.4 for the model ROM2.
8.4.1 - Model ROM3

- rectification section

\[ E_j^r = - \sum_{k=1}^{m+2} A_{j,k} V_k H_k^r - Z_R \sum_{i=1}^{nc} N_{i,j} \bar{H}_{i,j}^r - Z_R h_j^r a_{e_j} (T_j^r - T_j^r) (A_j)_R = 0 \]  
\[ j = 2,3,\ldots,m+2 \]  

\[ E_j^t = \sum_{k=1}^{m+2} A_{j,k} L_k H_k^t + Z_R \sum_{i=1}^{nc} N_{i,j} \bar{H}_{i,j}^t + Z_R h_j^t a_{e_j} (T_j^t - T_j^t) (A_j)_R = 0 \]  
\[ j = 1,2,\ldots,m+1 \]

\[ E_j^l = h_j^t a_{e_j} (T_j^t - T_j^l) (A_j)_R - h_j^t a_{e_j} (T_j^t - T_j^l) (A_j)_R + \sum_{i=1}^{nc} N_{i,j} \bar{H}_{i,j}^l = 0 \]  
\[ j = 1,2,\ldots,m+2 \]

\[ (R_j^r) = (R_j^r) ((\mathcal{N}_j)_l - (\mathcal{N}_j)_l) - c_{i,j} a_{e_j} ((\mathcal{N}_j)_l - (\mathcal{N}_j)_l) (A_j)_R = 0 \]  
\[ j = 1,2,\ldots,m+2 \]

\[ (R_j^t) = (R_j^t) ((\mathcal{N}_j)_l - (\mathcal{N}_j)_l) - c_{i,j} (\Gamma_{av})_l a_{e_j} ((\mathcal{N}_j)_l - (\mathcal{N}_j)_l) (A_j)_R = 0 \]  
\[ j = 1,2,\ldots,m+2 \]

- stripping section

The equations for the stripping section are similar to those for the rectification section [equations (8.17)-(8.21)] with the following modifications:

i. the index \( n \) replaces the index \( m \);

ii. the orthogonal collocation coefficients \( B_{i,k} \) (for \( n \) internal collocation points) replace the coefficients \( A_{i,k} \) (for \( m \) internal collocation points);

iii. the height of packing in the stripping section, \( Z_s \), replaces the height of packing in the rectification section, \( Z_r \);

iv. the cross sectional area of the column on the stripping section, \( (A)_s \), replaces the cross sectional area of the column on the enriching section, \( (A)_R \).
8.4.2- Model ROM4

- rectification section

\[ E_j^V = - \sum_{k=1}^{m+2} A_{j,k} V_k H_k^V - Z_R \sum_{i=1}^{\infty} N_{i,j} h_i^V \Xi_i^V a_r (T_j^V - T_i^V) (A_i)_R = 0 \] \hspace{1cm} j = 2,3,\ldots,m+2 \tag{8.22} 

\[ E_j^L = \sum_{k=1}^{m+2} A_{j,k} L_k H_k^L + Z_R \sum_{i=1}^{\infty} N_{i,j} h_i^L \Xi_i^L a_r (T_j^L - T_i^L) (A_i)_R = 0 \] \hspace{1cm} j = 1,2,\ldots,m+1 \tag{8.23} 

\[ E_j^L = h_j^V \Xi_j^V a_r (T_j^V - T_j^L) (A_j)_R - h_j^L \Xi_j^L a_r (T_j^L - T_j^L) (A_j)_R + \sum_{i=1}^{\infty} N_{i,j} h_i^L = 0 \] \hspace{1cm} j = 1,2,\ldots,m+2 \tag{8.24} 

\[ (R^V)_j = [R_{av}^V]_j \left( (N)_j - N_{t_j} (y)_j \right) - c_{t_j}^V [\Xi_0^V]_j a_{r_j} \left( (y)_j - (y')_j \right)(A_j)_R = (0) \] \hspace{1cm} j = 1,2,\ldots,m+2 \tag{8.25} 

\[ (R^L)_j = [R_{av}^L]_j \left( (N)_j - N_{t_j} (x)_j \right) - c_{t_j}^L [\Xi_0^L]_j a_{r_j} \left( (x)_j - (x')_j \right)(A_j)_R = (0) \] \hspace{1cm} j = 1,2,\ldots,m+2 \tag{8.26} 

- stripping section

The equations for the stripping section are similar to those for the rectification section [equations (8.17)-(8.21)] with the following modifications:

i. the index \( n \) replaces the index \( m \);  

ii. the orthogonal collocation coefficients \( B_{j,k} \) (for \( n \) internal collocation points) replace the coefficients \( A_{j,k} \) (for \( m \) internal collocation points);  

iii. the height of packing in the stripping section, \( Z_s \), replaces the height of packing in the rectification section, \( Z_r \);  

iv. the cross sectional area of the column on the stripping section, \( (A_s)_s \), replaces the cross sectional area of the column on the enriching section, \( (A_r)_r \).
8.5- NUMERICAL SOLUTION OF THE REDUCED-ORDER MODELS

8.5.1- Variables and equations at the collocation points
In both reduced-order models ROM3 and ROM4 there are 5nc+5 unknown variables at every collocation point and they are ordered in the vector \((x_i)\) as follows:

\[
(x_i)^T = (V_i, y_{1,i}, y_{2,i}, \cdots, y_{nc,i}, T_{y_i}^v, y_{1,i}^y, y_{2,i}^y, \cdots, y_{nc,i}^y, x_{1,i}, x_{2,i}, \cdots)
\]

\[
(x_i)^T = (x_{nc,i}, T_{x_i}^l, L_i, x_{1,i}, x_{2,i}, \cdots, x_{nc,i}, T_{x_i}^l, N_{1,i}, N_{2,i}, \cdots, N_{nc,i}) \quad (8.27)
\]

The corresponding 5nc+5 equations per collocation point are ordered in the vector \((f_i)\) as follows:

\[
(f_i)^T = (M_i^y, M_{1,i}^y, M_{2,i}^v, \cdots, M_{nc,i}^v, E_i^y, (R_y^v)^T, S_i^y, Q_i^l, Q_{2,i}, \cdots)
\]

\[
(f_i)^T = (Q_{nc,i}^l, E_i^l, M_{1,i}^l, M_{2,i}^v, \cdots, M_{nc,i}^v, E_i^l, (R_i^l)^T, S_i^l) \quad (8.28)
\]

8.5.2- Variables and equations for the packed column
The model for the entire column, considering \(n\) internal collocation points in the stripping section and \(m\) internal collocation points in the rectification section will have \((5nc+5)(n+m+4)+nc\) unknown variables and equations.

The variables will be collected in the vector \((x)\), starting from the reboiler and moving upwards in the column as follows:

\[
(x)^T = (x_{1,B}, x_{2,B}, \cdots, x_{nc,B}, (x_{1(n)})^T, (x_{2(n)})^T, \cdots, (x_{n+2})^T
\]

\[
((x_{1(m)})^T, (x_{2(m)})^T, \cdots, (x_{m+2})^T)
\]

\[
(x)^T = (x_{1,N}, x_{2,N}, \cdots, x_{nc,N}, (x_{1(n)})^T, (x_{2(n)})^T, \cdots, (x_{n+2})^T)
\]

\[
((x_{1(m)})^T, (x_{2(m)})^T, \cdots, (x_{m+2})^T)
\]

The ROM3 and ROM4 equations for the whole column are expressed in the general functional form
Chapter 8 - Reduced-Order Models 3 and 4 - ROM3 & ROM4

\[
(f(x))^T = (Q_{1B}, Q_{2B}, \ldots, Q_{mB}, (f_{1(m)})^T, (f_{2(m)})^T, \ldots, (f_{m+2})^T, (0)^T)
\]

(8.30)

It must be clear that, when using ROM3, for the stripping section of the column

- at collocation point 1 equations (7.55), (7.56), and (8.17) will be replaced by equations (7.77)-(7.79);
- at collocation point \(n+2\) equations (7.57), (7.58), and (8.18) will be replaced by equations (7.73)-(7.75);

and for the rectification section of the column

- at collocation point 1 equations (7.55), (7.56), and (8.17) will be replaced by equations (7.70)-(7.72);
- at collocation point \(m+2\) equations (7.57), (7.58), and (8.18) will be replaced by equations (7.67)-(7.69).

On the other hand, when using ROM4, for the stripping section of the column

- at collocation point 1 equations (7.55), (7.56), and (8.22) will be replaced by equations (7.77)-(7.79);
- at collocation point \(n+2\) equations (7.57), (7.58), and (8.23) will be replaced by equations (7.73)-(7.75);

and for the rectification section of the column

- at collocation point 1 equations (7.55), (7.56), and (8.22) will be replaced by equations (7.70)-(7.72);
- at collocation point \(m+2\) equations (7.57), (7.58), and (8.23) will be replaced by equations (7.67)-(7.69).

8.5.3- Solution of ROM3 and ROM4 equations
The system of algebraic equations represented by equation (8.30) was solved using the subroutine C05NDF already quoted in section 6.5.4.
9- CASE STUDY 1

9.1- INTRODUCTION
Having completed in the previous chapters the development of the four reduced-order models, the following three chapters will be devoted to the comparison of their strength. Three different case studies from the literature will be presented aiming to access the robustness of the models in achieving the solution of the examples.

9.2- SPECIFICATION OF THE PROBLEM
The first case study was used by some researchers for testing their models [von Rosenberg and Hadi (1980), Srivastava and Joseph (1984), and Wardle and Hapoglu (1992)]. The packed distillation column to be simulated is distilling an equimolar mixture of methyl cyclohexane (MCH), toluene (Tol), meta-xylene (m-Xyl), and para-xylene (p-Xyl). The column has an intermediate feed and is equipped with a total condenser and a partial reboiler. The complete set of specifications is presented in Table 9.1.

The previous simulations presented in the literature have been made with the equilibrium relationship based on constant relative volatilities for the components and with an overall mass transfer coefficient that remains constant for every section of the column. For the simulations presented in this chapter the equilibrium relationship adopted was more rigorous (see section 5.9) as was the procedure for the evaluation of the interphase mass transfer rates. Only the reduced-order model ROM1 relies on the use of overall mass transfer coefficients but they were allowed to change along the different sections of the column (while remaining the same for all the components).

9.3- INITIALISATION OF THE VARIABLES
To some extent the initialisation of the variables in the column followed the ideas presented by Krishnamurthy and Taylor (1985c) namely:
Table 9.1. Specifications for case study 1

<table>
<thead>
<tr>
<th>Section</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rectification section</td>
<td>Cross sectional area = 0.1 m²</td>
</tr>
<tr>
<td></td>
<td>Height of packing = 1.98 m</td>
</tr>
<tr>
<td>Stripping section</td>
<td>Cross sectional area = 0.1 m²</td>
</tr>
<tr>
<td></td>
<td>Height of packing = 1.98 m</td>
</tr>
<tr>
<td>Packing material</td>
<td>1/2&quot; Ceramic Raschig ring</td>
</tr>
<tr>
<td></td>
<td>Surface area = 368 m²/m³</td>
</tr>
<tr>
<td></td>
<td>Diameter = 12.7 mm</td>
</tr>
<tr>
<td>Feed condition</td>
<td>$T^F = 389.7$ K</td>
</tr>
<tr>
<td></td>
<td>$F^{VF} = 0.0$</td>
</tr>
<tr>
<td></td>
<td>$F^{LF} = 0.2483$ moles/s</td>
</tr>
<tr>
<td></td>
<td>$x_{MCH} = 0.25$</td>
</tr>
<tr>
<td></td>
<td>$x_{Tot} = 0.25$</td>
</tr>
<tr>
<td></td>
<td>$x_{m-xyl} = 0.25$</td>
</tr>
<tr>
<td></td>
<td>$x_{p-xyl} = 0.25$</td>
</tr>
<tr>
<td></td>
<td>$y_{MCH} = 0.00$</td>
</tr>
<tr>
<td></td>
<td>$y_{Tot} = 0.00$</td>
</tr>
<tr>
<td></td>
<td>$y_{m-xyl} = 0.00$</td>
</tr>
<tr>
<td></td>
<td>$y_{p-xyl} = 0.00$</td>
</tr>
<tr>
<td>Operation Pressure</td>
<td>$P = 1.0$ bar</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>$R_R = 5.0$</td>
</tr>
<tr>
<td>Bottom product flowrate</td>
<td>$B = 0.1216$ moles/s</td>
</tr>
</tbody>
</table>

- based on the guessed product compositions the temperatures at the top and at the bottom of the column are calculated using a bubble point temperature procedure;
- the temperatures at any other point in the column are obtained by linear interpolation of the end values. These temperatures will be considered the same for the liquid phase, the vapour phase, and for the interface;
- the liquid mole fractions are also obtained by linear interpolation of the end values. Whenever needed, the vapour mole fractions, the vapour mole fractions at the interface, and the liquid mole fractions at the interface are initialised with the same values as the liquid mole fractions;
- the total flowrates are estimated by assuming constant molar overflow in the various sections of the column;
- the mass transfer rates are initialised as being equal to one percent of the component flowrate at any specific location in the column. The signs for the
fluxes are assigned according to the components’ \( K \)-value. For \( K \)-values greater than one the fluxes are considered negative and for \( K \)-values smaller than one the fluxes are positive.

This initialisation procedure will also be used for case studies 2 and 3.

9.4- RESULTS FROM THE SIMULATIONS

This section will present the results of the simulation using the four reduced-order models together with some preliminary observations/conclusions. More general conclusions are left for chapter 12.

9.4.1- Overview

The results of the simulations using the models ROM1, ROM2, ROM3, and ROM4 with ten internal collocation points per section are presented in Figures 9.1 to 9.12. In these figures the 'doted' lines represent the profiles guessed at the beginning of the iterative process and the solid lines represent the solution found using the different models. The only exception is in Figure 9.2 because, due to the assumptions made on model ROM1, the guessed flowrate profiles are equal to the solution found using ROM1 (the 'solution' of the problem considering constant molar overflow).

There were some difficulties when using the model ROM1 with a small number of internal collocation points. Using two internal collocation points per section the model did not converge to a solution when using the initial values obtained by the procedure described in section 9.3. When the initial values were replaced by the solution obtained with the model ROM3 (with two internal collocation points per section) the solution with ROM1 was then obtained. Adopting three internal collocation points per section there were no problems in obtaining the solution with ROM1 but it was not possible to obtain the convergence on the values of the overall mass transfer coefficients as described in section 6.5.
Chapter 9 - Case Study 1

Figure 9.1. Comparison between the initial profiles (o o o) and the profiles obtained using ROM1 with n=m=10 (—) for example 1. Liquid mole fraction profiles.

Figure 9.2. Comparison between the initial profiles (o o o) and the profiles obtained using ROM1 with n=m=10 (—) for example 1. Temperature and flowrate profiles.
Figure 9.3. Comparison between the initial profiles (o o o) and the profiles obtained using ROM1 with n=m=10 (—) for example 1. Interphase mass transfer rate profiles.

Figure 9.4. Comparison between the initial profiles (o o o) and the profiles obtained using ROM2 with n=m=10 (—) for example 1. Liquid mole fraction profiles.
Figure 9.5. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM2 with \( n=m=10 \) (——) for example 1. Temperature and flowrate profiles.

Figure 9.6. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM2 with \( n=m=10 \) (——) for example 1. Interphase mass transfer rate profiles.
Figure 9.7. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM3 with $n=m=10$ (——) for example 1. Liquid mole fraction profiles.

Figure 9.8. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM3 with $n=m=10$ (——) for example 1. Temperature and flowrate profiles.
Figure 9.9. Comparison between the initial profiles (o o o) and the profiles obtained using ROM3 with $n=m=10$ (—) for example 1. Interphase mass transfer rate profiles.

Figure 9.10. Comparison between the initial profiles (o o o) and the profiles obtained using ROM4 with $n=m=10$ (—) for example 1. Liquid mole fraction profiles.
Figure 9.11. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM4 with n=m=10 (— ) for example 1. Temperature and flowrate profiles.

Figure 9.12. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM4 with n=m=10 (— ) for example 1. Interphase mass transfer rate profiles.
A summary of the results obtained in the simulations of example 1 with the reduced-order models is presented in Table 9.2. The key for this table is:

1. Normal. The solution of the problem was found with the initial values obtained using the procedure presented in section 9.3;
2. The solution of the problem was obtained but only when using as initial values the results obtained with the reduced-order model ROM3;
3. Failed. It was not possible to find the solution of the problem;
4. The solution of the system of algebraic equations of the model was found, however there was no convergence on the values of the overall mass transfer coefficients (see section 6.5). This entry is specific for the model ROM1.

<table>
<thead>
<tr>
<th></th>
<th>ROM1</th>
<th>ROM2</th>
<th></th>
<th>ROM3</th>
<th>ROM4</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = m = 2</td>
<td>2</td>
<td>n = m = 2</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n = m = 3</td>
<td>4</td>
<td>n = m = 3</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n = m = 4</td>
<td>1</td>
<td>n = m = 4</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n = m = 6</td>
<td>1</td>
<td>n = m = 6</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n = m = 10</td>
<td>1</td>
<td>n = m = 10</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

9.4.2- Influence of the number of collocation points

The effect of increasing the number of internal collocation points employed in the approximation was investigated. Some results are presented in Figures 9.13 to 9.21. As it was already reported by Srivastava and Joseph (1984) the solution was found to converge rapidly with respect to the number of collocation points, particularly at the ends of the column.
Figure 9.13. ROM1 - Comparison between the solution obtained with \( n=m=2 \) (○ ○ ○) and the solution obtained using \( n=m=10 \) (——) for example 1. Liquid mole fraction profiles.

Figure 9.14. ROM1 - Comparison between the solution obtained with \( n=m=2 \) (○ ○ ○) and the solution obtained using \( n=m=10 \) (——) for example 1. Temperature profiles.
Figure 9.15. ROM1 - Comparison between the solution obtained with \( n=m=2 \) (○ ○ ○) and the solution obtained using \( n=m=10 \) (—) for example 1. Interphase mass transfer rate profiles.

Figure 9.16. ROM2 - Comparison between the solution obtained with \( n=m=2 \) (○ ○ ○) and the solution obtained using \( n=m=10 \) (—) for example 1. Liquid mole fraction profiles.
Figure 9.17. ROM2 - Comparison between the solution obtained with $n=m=2$ (○ ○ ○) and the solution obtained using $n=m=10$ (-----) for example 1. Temperature and flowrate profiles.

Figure 9.18. ROM2 - Comparison between the solution obtained with $n=m=2$ (○ ○ ○) and the solution obtained using $n=m=10$ (-----) for example 1. Interphase mass transfer rate profiles.
Figure 9.19. ROM4 - Comparison between the solution obtained with \( n=m=2 \) (○ ○ ○) and the solution obtained using \( n=m=10 \) (—) for example 1. Liquid mole fraction profiles.

Figure 9.20. ROM4 - Comparison between the solution obtained with \( n=m=2 \) (○ ○ ○) and the solution obtained using \( n=m=10 \) (—) for example 1. Temperature and flowrate profiles.
Figure 9.21. ROM4 - Comparison between the solution obtained with $n=m=2$ (○ ○ ○) and the solution obtained using $n=m=10$ (---) for example 1. Interphase mass transfer rate profiles.

It is worth noticing that, again, the model that had the worst performance when using a small number of collocation points in the approximation, was the reduced-order model ROM1.

9.4.3- Comparison of the models
In this section the results obtained from the four different models are compared. The comparison was made using the solutions found with ten internal collocation points per section. The results from models ROM1, ROM2, and ROM3 will be compared with those obtained with the more rigorous of the reduced-order models, model ROM4.

In Figures 9.22 to 9.30 one can find graphs comparing the profiles computed with the models. It is interesting to observe that despite the differences in all the profiles computed with models ROM1 and ROM4, there was a good agreement on the composition of the products predicted by both models.
Figure 9.22. Comparison between the solution for example 1 obtained with model ROM1 (○○○) and the solution obtained with model ROM4 (----). Liquid mole fraction profiles (n=m=10).

Figure 9.23. Comparison between the solution for example 1 obtained with model ROM1 (○○○) and the solution obtained with model ROM4 (----). Temperature and flowrate profiles (n=m=10).
**Figure 9.24.** Comparison between the solution for example 1 obtained with model ROM1 (○ ○ ○) and the solution obtained with model ROM4 (---). Interphase mass transfer rate profiles \((n=m=10)\).

**Figure 9.25.** Comparison between the solution for example 1 obtained with model ROM2 (○ ○ ○) and the solution obtained with model ROM4 (---). Liquid mole fraction profiles \((n=m=10)\).
**Figure 9.26.** Comparison between the solution for example 1 obtained with model ROM2 (○ ○ ○) and the solution obtained with model ROM4 (---). Temperature and flowrate profiles \((n=m=10)\).

**Figure 9.27.** Comparison between the solution for example 1 obtained with model ROM2 (○ ○ ○) and the solution obtained with model ROM4 (---). Interphase mass transfer rate profiles \((n=m=10)\).
Chapter 9 - Case Study 1

4.0
3.0
2.0
1.0
0.0
0.10 0.20 0.30 0.40 0.50
0.00

Figure 9.28. Comparison between the solution for example 1 obtained with model ROM3 (○ ○ ○) and the solution obtained with model ROM4 (—). Liquid mole fraction profiles (n=m=10).

Flowrate, moles/s

4.0
3.0
2.0
1.0
0.56 0.60 0.65 0.70 0.75 0.80 0.85 0.90

Figure 9.29. Comparison between the solution for example 1 obtained with model ROM3 (○ ○ ○) and the solution obtained with model ROM4 (—). Temperature and flowrate profiles (n=m=10).
Figure 9.30. Comparison between the solution for example 1 obtained with model ROM3 (○ ○ ○) and the solution obtained with model ROM4 (—). Interphase mass transfer rate profiles \(n=m=10\).

One can observe from Figures 9.28 to 9.30 that there was no significant difference between the results obtained using models ROM3 and ROM4. The comparison between models ROM2 and ROM4 (see Figures 9.25 to 9.27) indicated minor differences only on the liquid and vapour flowrate profiles while all the other predictions do agree remarkably well.

As the results obtained using the models ROM2, ROM3, and ROM4 were basically the same it became even more important to analyse the difficulties encountered on the process of solving the system of algebraic equations of the different models.

In Figures 9.31 to 9.35 the evolution of the Euclidean norm of the vector of functions with the number of iterations is presented for models ROM2, ROM3, and ROM4 for different approximations. In these plots the arrows indicate that a new Jacobian evaluation was needed to proceed towards the solution of the problem. The CPU time spent in the simulations is presented in Appendix 3.
**Figure 9.31.** Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 1 with ten internal collocation points per section.

**Figure 9.32.** Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 1 with six internal collocation points per section.
Figure 9.33. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 1 with four internal collocation points per section.

Figure 9.34. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 1 with three internal collocation points per section.
9.5- PRELIMINARY CONCLUSIONS

Considering the results of the simulations some preliminary conclusions can be drawn:

- a small number of internal collocation points can be used when one is interested only on the results at the top and bottom of the column. This is because the solution at these points converges very rapidly with respect to the number of collocation points.

- There was a balance in the performance of the models ROM2, ROM3, and ROM4. The three models gave essentially the same results but when using a small number of collocation points the models ROM3 and ROM4 outperformed model ROM2. The opposite happened for a large number of collocation points.
Chapter 10 - Case Study 2

10- CASE STUDY 2

10.1- SPECIFICATION OF THE PROBLEM

The second case study deals with an industrial depropanizer, which uses structured packing and was originally presented by Wang and Cameron (1991). The packed distillation column to be simulated is distilling a multicomponent mixture of ethane (C2), propane (C3), propylene (C3=), and isobutane (i-C4). The column has an intermediate feed and is equipped with a total condenser and a partial reboiler. The complete set of specifications is presented in Table 10.1.

\textit{Table 10.1. Specifications for case study 2}

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rectification section</td>
<td>Cross sectional area = 0.65 m$^2$</td>
</tr>
<tr>
<td></td>
<td>Height of packing = 4.08 m</td>
</tr>
<tr>
<td>Stripping section</td>
<td>Cross sectional area = 0.65 m$^2$</td>
</tr>
<tr>
<td></td>
<td>Height of packing = 4.08 m</td>
</tr>
<tr>
<td>Packing material</td>
<td>Mellapak 250Y</td>
</tr>
<tr>
<td></td>
<td>Surface area = 250 m$^2$/ m$^3$</td>
</tr>
<tr>
<td></td>
<td>Void fraction = 0.95</td>
</tr>
<tr>
<td></td>
<td>Angle of flow channel = 45°</td>
</tr>
<tr>
<td></td>
<td>Crimp height = 0.0119 m</td>
</tr>
<tr>
<td></td>
<td>Channel side = 0.0171 m</td>
</tr>
<tr>
<td></td>
<td>Channel base = 0.0241 m</td>
</tr>
<tr>
<td>Feed condition</td>
<td>$T^F = 344.2$ K</td>
</tr>
<tr>
<td></td>
<td>$F^{VF} = 69.56$ moles/s</td>
</tr>
<tr>
<td></td>
<td>$F^{LF} = 2.38$ moles/s</td>
</tr>
<tr>
<td></td>
<td>$x_{C2} = 0.005$</td>
</tr>
<tr>
<td></td>
<td>$x_{C3} = 0.075$</td>
</tr>
<tr>
<td></td>
<td>$x_{C3=} = 0.190$</td>
</tr>
<tr>
<td></td>
<td>$x_{i-C4} = 0.730$</td>
</tr>
<tr>
<td></td>
<td>$y_{C2} = 0.026$</td>
</tr>
<tr>
<td></td>
<td>$y_{C3} = 0.119$</td>
</tr>
<tr>
<td></td>
<td>$y_{C3=} = 0.354$</td>
</tr>
<tr>
<td></td>
<td>$y_{i-C4} = 0.501$</td>
</tr>
<tr>
<td>Operation Pressure</td>
<td>$P = 16.5$ bar</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>$R_R = 3.75$</td>
</tr>
<tr>
<td>Bottom product flowrate</td>
<td>$B = 41.68$ moles/s</td>
</tr>
</tbody>
</table>
10.2- INITIALISATION OF THE VARIABLES
The initialisation of the variables followed the procedure outlined in section 9.3.

10.3- RESULTS FROM THE SIMULATIONS
This section will present the results of the simulation using the four reduced-order models together with some preliminary observations/conclusions. More general conclusions are left for chapter 12.

10.3.1- Overview
The results of the simulations using the models ROM1, ROM2, ROM3, and ROM4 with ten internal collocation points per section are presented in Figures 10.1 to 10.12. In these figures the 'dotted' lines represent the profiles guessed at the beginning of the iterative process and the solid lines represent the solution found using the different models. The only exception is in Figure 10.2 because, due to the assumptions made on model ROM1, the guessed flowrate profiles are equal to the solution found using ROM1 (the 'solution' of the problem considering constant molar overflow).

There were some difficulties when using the models ROM1 and ROM2. The solution of the system of algebraic equations was always found when using the model ROM1 although, for two, four, and six internal collocation points per section it was not possible to obtain the convergence on the overall mass transfer coefficients.

The problem with the model ROM2 was more severe. When using six internal collocation points per section the model did not converge to a solution when starting from the initial values obtained by the procedure described in section 9.3. When the initial values were replaced by the solution obtained with the model ROM3 (with six internal collocation points per section) the solution with ROM2 was then obtained.
Figure 10.1. Comparison between the initial profiles (○○○) and the profiles obtained using ROM1 with n=m=10 (——) for example 2. Liquid mole fraction profiles.

Figure 10.2. Comparison between the initial profiles (○○○) and the profiles obtained using ROM1 with n=m=10 (——) for example 2. Temperature and flowrate profiles.
Figure 10.3. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM1 with \( n=m=10 \) (——) for example 2. Interphase mass transfer rate profiles. \( \triangle \) collocation points employed.

Figure 10.4. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM2 with \( n=m=10 \) (——) for example 2. Liquid mole fraction profiles.
Chapter 10 - Case Study 2

Figure 10.5. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM2 with n=m=10 (-----) for example 2. Temperature and flowrate profiles. △ collocation points employed.

Figure 10.6. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM2 with n=m=10 (-----) for example 2. Interphase mass transfer rate profiles.
Figure 10.7. Comparison between the initial profiles (o o o) and the profiles obtained using ROM3 with n=m=10 (---) for example 2. Liquid mole fraction profiles.

Figure 10.8. Comparison between the initial profiles (o o o) and the profiles obtained using ROM3 with n=m=10 (---) for example 2. Temperature and flowrate profiles.
Chapter 10 - Case Study 2

Figure 10.9. Comparison between the initial profiles (○○○) and the profiles obtained using ROM3 with \( n=m=10 \) (—) for example 2. Interphase mass transfer rate profiles.

Figure 10.10. Comparison between the initial profiles (○○○) and the profiles obtained using ROM4 with \( n=m=10 \) (—) for example 2. Liquid mole fraction profiles.
**Figure 10.11.** Comparison between the initial profiles (○○○) and the profiles obtained using ROM4 with n=m=10 (—) for example 2. Temperature and flowrate profiles.

**Figure 10.12.** Comparison between the initial profiles (○○○) and the profiles obtained using ROM4 with n=m=10 (—) for example 2. Interphase mass transfer rate profiles.
A summary of the results obtained in the simulations of example 2 with the reduced-order models is presented in Table 10.2. The key for this table is the same as the one for Table 9.2 presented in section 9.4.1.

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</table>

<table>
<thead>
<tr>
<th></th>
<th>ROM3</th>
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<td>1</td>
<td>$n = m = 10$</td>
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</tr>
</tbody>
</table>

### 10.3.2- Influence of the number of collocation points

The effect of increasing the number of internal collocation points employed in the approximation was investigated. Some results are presented in Figures 10.13 to 10.21 where the solutions obtained with ten internal collocation points are compared with those obtained with three internal collocation points per section.

The solution was found to converge rapidly with respect to the number of collocation points for the models ROM2, ROM3, and ROM4 (particularly at the ends of the column), although it was not as rapid as it was for example 1. The solution also converged with respect to the number of collocation points for the model ROM1 but at a much smaller rate. In addition to this, for a small number of collocation points, the solution with ROM1 indicated the lighter component to be concentrated in the wrong end of the column.
Figure 10.13. ROM1 - Comparison between the solution obtained with \( n=m=3 \) (○ ○ ○) and the solution obtained using \( n=m=10 \) (—) for example 2. Liquid mole fraction profiles.

Figure 10.14. ROM1 - Comparison between the solution obtained with \( n=m=3 \) (○ ○ ○) and the solution obtained using \( n=m=10 \) (—) for example 2. Temperature profiles.
Figure 10.15. ROM1 - Comparison between the solution obtained with $n=m=3$ (○ ○ ○) and the solution obtained using $n=m=10$ (—) for example 2. Interphase mass transfer rate profiles.

Figure 10.16. ROM2 - Comparison between the solution obtained with $n=m=3$ (○ ○ ○) and the solution obtained using $n=m=10$ (—) for example 2. Liquid mole fraction profiles.
Figure 10.17. ROM2 - Comparison between the solution obtained with $n=m=3$ (○ ○ ○) and the solution obtained using $n=m=10$ (——) for example 2. Temperature and flowrate profiles.

Figure 10.18. ROM2 - Comparison between the solution obtained with $n=m=3$ (○ ○ ○) and the solution obtained using $n=m=10$ (——) for example 2. Interphase mass transfer rate profiles.
Figure 10.19. ROM4 - Comparison between the solution obtained with $n=m=3$ (○ ○ ○) and the solution obtained using $n=m=10$ (—) for example 2. Liquid mole fraction profiles.

Figure 10.20. ROM4 - Comparison between the solution obtained with $n=m=3$ (○ ○ ○) and the solution obtained using $n=m=10$ (—) for example 2. Temperature and flowrate profiles.
10.3.3- Comparison of the models

In this section the results obtained from the four different models are compared. The comparison was made using the solutions found with ten internal collocation points per section. The results from models ROM1, ROM2, and ROM3 will be compared with those obtained with the more rigorous of the reduced-order models, model ROM4.

In Figures 10.22 to 10.30 one can find graphs comparing the profiles computed with the models. As happened with example 1, despite the differences in all the profiles computed with models ROM1 and ROM4, there was a reasonable agreement in the composition of the products predicted by both models (see Figure 10.22).

The comparison between models ROM2 and ROM4 (see Figures 10.25 to 10.27) indicated some differences on the liquid and vapour flowrate profiles,
Figure 10.22. Comparison between the solution for example 2 obtained with model ROM1 (○○○) and the solution obtained with model ROM4 (—). Liquid mole fraction profiles (n=m=10).

Figure 10.23. Comparison between the solution for example 2 obtained with model ROM1 (○○○) and the solution obtained with model ROM4 (—). Temperature profiles (n=m=10).
Figure 10.24. Comparison between the solution for example 2 obtained with model ROM1 (○ ○ ○) and the solution obtained with model ROM4 (—). Interphase mass transfer rate profiles (n=m=10).

Figure 10.25. Comparison between the solution for example 2 obtained with model ROM2 (○ ○ ○) and the solution obtained with model ROM4 (—). Liquid mole fraction profiles (n=m=10).
Figure 10.26. Comparison between the solution for example 2 obtained with model ROM2 (o o o) and the solution obtained with model ROM4 (---). Temperature and flowrate profiles (n=m=10).

Figure 10.27. Comparison between the solution for example 2 obtained with model ROM2 (o o o) and the solution obtained with model ROM4 (---). Interphase mass transfer rate profiles (n=m=10).
**Figure 10.28.** Comparison between the solution for example 2 obtained with model ROM3 (○ ○ ○) and the solution obtained with model ROM4 (—). Liquid mole fraction profiles (n=m=10).

**Figure 10.29.** Comparison between the solution for example 2 obtained with model ROM3 (○ ○ ○) and the solution obtained with model ROM4 (—). Temperature and flowrate profiles (n=m=10).
Figure 10.30. Comparison between the solution for example 2 obtained with model ROM3 (○ ○ ○) and the solution obtained with model ROM4 (——). Interphase mass transfer rate profiles (n=m=10).

particularly the vapour flowrate in the stripping section. All the other predictions do agree remarkably well.

One can observe from Figures 10.28 to 10.30 that there was no significant difference between the results obtained using models ROM3 and ROM4.

The similarity between the results obtained using the models ROM3 and ROM4 together with the small differences between these results and those obtained with the model ROM2 indicated the need to investigate any possible problem in solving the system of algebraic equations of the different models.

In Figures 10.31 to 10.35 the evolution of the Euclidean norm of the vector of functions with the number of iterations is presented for models ROM2, ROM3, and ROM4 for different approximations. Again, the arrows indicate that a new Jacobian was evaluated to allow a further minimisation of the Euclidean norm of the vector of functions. The ‘dotted’ curves in Figure 10.32 represent the
Figure 10.31. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 2 with ten internal collocation points per section.

Figure 10.32. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 2 with six internal collocation points per section.
Figure 10.33. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 2 with four internal collocation points per section.

Figure 10.34. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 2 with three internal collocation points per section.
results obtained when the solution from the simulation with model ROM3 are used as the initial values. The CPU time spent in the simulations is presented in Appendix 3.

10.4- PRELIMINARY CONCLUSIONS
Considering the results of the simulations some preliminary conclusions can be drawn:
- as happened before, a small number of internal collocation points can be used when one is interested only on the results at the top and bottom of the column (except when using the model ROM1).

There was barely any difference in the performance of models ROM3 and ROM4 and they outperformed the model ROM2. The three models gave approximately the same results but the model ROM2 always needed some extra Jacobian evaluations and, for six internal collocation points, it did fail to find the solution when starting from the linear profiles.
11- CASE STUDY 3

11.1- SPECIFICATION OF THE PROBLEM

The third and final case study is an adaptation of a problem presented by Taylor and Krishna (1993). The original problem was to design a tray column to separate n-propane from n-butane in a four component mixture. The final design led to a column equipped with 14 trays in the rectification section, 19 trays in the stripping section, a partial condenser, and a partial reboiler. In the present simulation the trays were substituted by structured packing (Mellapack 250Y) and the partial condenser was replaced by a total condenser. The complete set of specifications is presented in Table 11.1.

Table 11.1. Specifications for case study 3

<table>
<thead>
<tr>
<th>Specification</th>
<th>Values</th>
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<tbody>
<tr>
<td>Rectification section</td>
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<tr>
<td>Cross sectional area</td>
<td>2.14 m²</td>
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<tr>
<td>Height of packing</td>
<td>3.66 m</td>
</tr>
<tr>
<td>Stripping section</td>
<td></td>
</tr>
<tr>
<td>Cross sectional area</td>
<td>2.14 m²</td>
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<tr>
<td>Height of packing</td>
<td>4.34 m</td>
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<td>Packing material</td>
<td>Mellapak 250Y</td>
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<td>Surface area</td>
<td>250 m²/m³</td>
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<td>Void fraction</td>
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<td>Angle of flow channel</td>
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<td>$B$</td>
<td>600.00 moles/s</td>
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</table>
11.2- Initialisation of the Variables

The initialisation of the variables followed the procedure outlined in section 9.3.

11.3- Results from the Simulations

This section will present the results of the simulation using the four reduced-order models together with some preliminary observations/conclusions. More general conclusions are left for chapter 12.

11.3.1- Overview

The results of the simulations using the models ROM1, ROM3, and ROM4 with ten internal collocation points per section and using the model ROM2 with six internal collocation points per section are presented in Figures 11.1 to 11.12. In these figures the 'dotted' lines represent the profiles guessed at the beginning of the iterative process and the solid lines represent the solution found using the different models. The only exception is in Figure 11.2 because, due to the assumptions made on model ROM1, the guessed flowrate profiles are equal to the solution found using ROM1 (the 'solution' of the problem considering constant molar overflow).

There were several problems when using the models ROM1 and ROM2. When the model ROM1 was used with two or four internal collocation points per section it was not possible to find the solution of the problem. When the number of internal collocation points was three, six, or ten a solution was found but the convergence on the overall mass transfer coefficients was unattainable.

The problem with the model ROM2 happened when the solution was tried with six or ten internal collocation points per section. For these situations the model did not converge to a solution neither starting from the initial values obtained by the procedure described in section 9.3 nor when the initial values were replaced by the solution obtained with the model ROM3 (with six or ten internal collocation points per section, respectively). The behaviour of the system was
Chapter 11 - Case Study 3

Figure 11.1. Comparison between the initial profiles (● ● ●) and the profiles obtained using ROM1 with \( n=m=10 \) (——) for example 3. Liquid mole fraction profiles.

Figure 11.2. Comparison between the initial profiles (● ● ●) and the profiles obtained using ROM1 with \( n=m=10 \) (——) for example 3. Temperature and flowrate profiles.
Chapter 11 - Case Study 3

**Figure 11.3.** Comparison between the initial profiles (o o o) and the profiles obtained using ROM1 with $n=m=10$ (---) for example 3. Interphase mass transfer rate profiles.

**Figure 11.4.** Comparison between the initial profiles (o o o) and the profiles obtained using ROM2 with $n=m=6$ (---) for example 3. Liquid mole fraction profiles.
Figure 11.5. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM2 with $n=m=6$ (—) for example 3. Temperature and flowrate profiles.

Figure 11.6. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM2 with $n=m=6$ (—) for example 3. Interphase mass transfer rate profiles.
Figure 11.7. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM3 with \( n=m=10 \) (—) for example 3. Liquid mole fraction profiles.

Figure 11.8. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM3 with \( n=m=10 \) (—) for example 3. Temperature and flowrate profiles.
Figure 11.9. Comparison between the initial profiles (o o o) and the profiles obtained using ROM3 with n=m=10 (—) for example 3. Interphase mass transfer rate profiles.

Figure 11.10. Comparison between the initial profiles (o o o) and the profiles obtained using ROM4 with n=m=10 (—) for example 3. Liquid mole fraction profiles.
Figure 11.11. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM4 with $n=m=10$ (—) for example 3. Temperature and flowrate profiles.

Figure 11.12. Comparison between the initial profiles (○ ○ ○) and the profiles obtained using ROM4 with $n=m=10$ (—) for example 3. Interphase mass transfer rate profiles.
slightly better when working with six internal collocation points as, despite not reaching the solution of the problem, the Euclidean norm of the vector of functions was significantly reduced from its initial value when the results from ROM3 were used as the starting point. These are the values presented in Figures 11.4 to 11.6.

A summary of the results obtained in the simulations of example 3 with the reduced-order models is presented in Table 11.2. The key for this table is the same as the one for Table 9.2 presented in section 9.4.1.

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<th>Table 11.2. Example 3 - Summary of results.</th>
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<table>
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</table>

11.3.2- Influence of the number of collocation points
The effect of increasing the number of internal collocation points employed in the approximation was investigated. Some results are presented in Figures 11.13 to 11.21 where the solutions obtained with ten internal collocation points per section (six internal collocation points per section for the simulations with model ROM2) are compared with those obtained with three internal collocation points.
Figure 11.13. ROM1 - Comparison between the solution obtained with $n=m=3$ (○ ○ ○) and the solution obtained using $n=m=10$ (— ) for example 3. Liquid mole fraction profiles.

Figure 11.14. ROM1 - Comparison between the solution obtained with $n=m=3$ (○ ○ ○) and the solution obtained using $n=m=10$ (— ) for example 3. Temperature profiles.
Figure 11.15. ROM1 - Comparison between the solution obtained with n=m=3 (o o o) and the solution obtained using n=m=10 (— ) for example 3. Interphase mass transfer rate profiles.

Figure 11.16. ROM2 - Comparison between the solution obtained with n=m=3 (o o o) and the solution obtained using n=m=6 (— ) for example 3. Liquid mole fraction profiles.
Figure 11.17. ROM2 - Comparison between the solution obtained with \( n=m=3 \) (○ ○ ○) and the solution obtained using \( n=m=6 \) (——) for example 3. Temperature and flowrate profiles.

Figure 11.18. ROM2 - Comparison between the solution obtained with \( n=m=3 \) (○ ○ ○) and the solution obtained using \( n=m=6 \) (——) for example 3. Interphase mass transfer rate profiles.
Figure 11.19. ROM4 - Comparison between the solution obtained with $n=m=3$ (●●●) and the solution obtained using $n=m=10$ (—) for example 3. Liquid mole fraction profiles.

Figure 11.20. ROM4 - Comparison between the solution obtained with $n=m=3$ (●●●) and the solution obtained using $n=m=10$ (—) for example 3. Temperature and flowrate profiles.
Figure 11.21. ROM4 - Comparison between the solution obtained with \( n=m=3 \) (○ ○ ○) and the solution obtained using \( n=m=10 \) (——) for example 3. Interphase mass transfer rate profiles.

The solution was found to converge rapidly with respect to the number of collocation points for the models ROM3, and ROM4 (particularly at the ends of the column). This seemed to be the trend for the model ROM2 as well although it was not fully verified as the solution with six and ten internal collocation points per section was not achieved. The solution also converged with respect to the number of collocation points for the model ROM1 but at a much smaller rate.

### 11.3.3- Comparison of the models

In this section the results obtained from the four different models are compared. The comparison was made using the solutions found with six internal collocation points per section (as there was no solution from model ROM2 when using ten internal collocation points per section). The results from models ROM1, ROM2, and ROM3 will be compared with those obtained with the more rigorous of the reduced-order models, model ROM4.
In Figures 11.22 to 11.30 one will find graphs comparing the profiles computed with the different models. As happened with examples 1 and 2, despite the differences in all the profiles computed with models ROM1 and ROM4, there was a good agreement in the composition of the products predicted by both models (see Figure 11.22).

The comparison between models ROM2 and ROM4 (see Figures 11.25 to 11.27) indicated some differences on the liquid and vapour flowrate profiles. All the other predictions did agree remarkably well.

There was no significant difference between the results obtained using models ROM3 and ROM4 as one can observe from Figures 11.28 to 11.30.

The similarity between the results obtained using the models ROM3 and ROM4 together with the small differences between these results and those obtained with the model ROM2 triggered the investigation of any possible difficulties on the simulation using the different models.

![Graph showing liquid mole fraction profiles](image)

**Figure 11.22.** Comparison between the solution for example 3 obtained with model ROM1 (○ ○ ○) and the solution obtained with model ROM4 (— —). Liquid mole fraction profiles (n=m=6).
Figure 11.23. Comparison between the solution for example 3 obtained with model ROM1 (○ ○ ○) and the solution obtained with model ROM4 (—). Temperature profiles (n=m=6).

Figure 11.24. Comparison between the solution for example 3 obtained with model ROM1 (○ ○ ○) and the solution obtained with model ROM4 (—). Interphase mass transfer rate profiles (n=m=6).
**Figure 11.25.** Comparison between the solution for example 3 obtained with model ROM2 (○ ○ ○) and the solution obtained with model ROM4 (---). Liquid mole fraction profiles (n=m=6).

**Figure 11.26.** Comparison between the solution for example 3 obtained with model ROM2 (○ ○ ○) and the solution obtained with model ROM4 (---). Temperature and flowrate profiles (n=m=6).
**Figure 11.27.** Comparison between the solution for example 3 obtained with model ROM2 (○○○) and the solution obtained with model ROM4 (——). Interphase mass transfer rate profiles (n=m=6).

**Figure 11.28.** Comparison between the solution for example 3 obtained with model ROM3 (○○○) and the solution obtained with model ROM4 (——). Liquid mole fraction profiles (n=m=6).
**Figure 11.29.** Comparison between the solution for example 3 obtained with model ROM3 (○ ○ ○) and the solution obtained with model ROM4 (—). Temperature and flowrate profiles (n=m=6).

**Figure 11.30.** Comparison between the solution for example 3 obtained with model ROM3 (○ ○ ○) and the solution obtained with model ROM4 (—). Interphase mass transfer rate profiles (n=m=6).
In order to assess the rate of convergence for the different models the Euclidean norm of the vector of functions was plotted versus the number of iterations for models ROM2, ROM3, and ROM4. In Figures 11.31 to 11.35 one can find this information for the different approximations tested. Again, the arrows indicate that a new Jacobian was evaluated to allow a further minimisation of the Euclidean norm of the vector of functions. The 'dotted' curves in Figures 11.31 and 11.32 represent the results obtained with model ROM2 using starting values produced by model ROM3. The CPU time spent in the simulations is presented in Appendix 3.

11.4- PRELIMINARY CONCLUSIONS

Considering the results of the simulations some preliminary conclusions can be drawn:

• as happened before, if one is only interested in the products’ compositions a small number of internal collocation points can be used on the approximation (except when using the model ROM1).

![Figure 11.31. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 3 with ten internal collocation points per section.](image-url)
Figure 11.32. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 3 with six internal collocation points per section.

Figure 11.33. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 3 with four internal collocation points per section.
Figure 11.34. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 3 with three internal collocation points per section.

Figure 11.35. Evolution of the Euclidean norm of the vector of functions with the iteration number. Solutions of example 3 with two internal collocation points per section.
There was almost no difference in performance between the models ROM3 and ROM4. The results produced by these two models and by the model ROM2 were in very good agreement. The models ROM3 and ROM4 outperformed the model ROM2 in all the simulations but the one using two internal collocation points per section. This, added to the failure of model ROM2 in producing a solution using six and ten internal collocation points per section, indicated models ROM3 and ROM4 as the chosen models for the simulation of this example.
12- CONCLUSIONS AND FUTURE WORK

12.1- Mass Transfer Models
The reduced-order models developed and tested in this work were based on three different approaches for the evaluation of the interphase mass transfer rates, namely:

- the linearised theory of Toor-Stewart-Prober (models ROM3 and ROM4);
- an effective diffusivity approach based on the definition presented by Bird et al. (1960) (model ROM2);
- a simplified approach based on the assumption of equimolar counterflow and on the existence of a unique overall mass transfer coefficient for all the components present in the mixture (model ROM1).

In their statistical comparison of mass transfer models, Smith and Taylor (1983) did not include Bird's effective diffusivity formulation. Their results for nonequimolar distillation of nonideal mixtures (pentane, ethanol, and water or methanol, ethanol, and water) indicated poor performance of some simplifications in Bird's formulation.

In the light of the three case studies presented in this work one can draw the following conclusions:

- Despite predicting the right tendency for the mass transfer rates in case study 1, in general, the simplified approach employed in the model ROM1 can not be considered as a reasonable alternative for the computation of the interphase mass transfer rates.

- From the mass transfer point of view there was no significant difference between the results predicted using models ROM2, ROM3, and ROM4, therefore the effective diffusivity approach was a good approximation for the simulated systems. This was not completely unexpected as the mixtures involved in the case studies consisted of components of a similar nature, a situation in which the interaction effects are not expected to play a major role. In order to have a more complete picture of the reliability of this effective diffusivity approach, the model ROM2 would have to be
tested simulating systems involving mixtures of a more demanding nature.

- The absence of significant differences between the predictions from models ROM3 and ROM4 indicated that there was no need to take into account the high flux correction factors for the mass transfer coefficients. In other words, the matrix of high flux correction factors, \( [\Xi] \), is very well approximated by the identity matrix, \( [I] \). The results presented in this work confirm the findings of Powers et al. (1988). They indicated that, in general, for the simulation of distillation columns one can neglect the high flux correction factors. In the simulations presented in this work this would represent a saving of approximately ten percent of the computing time needed for the simulations neglecting the correction factors.

12.2- Initialisation of the Vector of Unknown Variables \((\vec{x})\)

Krishnamurthy and Taylor (1985c) have stressed the need for an "unusually good initial estimate of the variables" as a requirement for the convergence of the numerical algorithm for the nonequilibrium stage model. Their initialisation procedure included a single iteration of the Wang and Henke (see chapter 2) method of solving the equilibrium stage model equations to compute the compositions of each phase. They have used ideal \( K \)-values in these computations. The remaining variables were initialised using a similar procedure to the one used in the three case studies presented in chapters 9, 10, and 11. The authors report that their initialisation procedure did not provide sufficiently good estimates of the variables in several instances, particularly when the number of stages was large. Some 'nursing' techniques used to obtain convergence in some difficult cases were presented by Krishnamurthy and Taylor (1985c) and by Powers et al. (1988).

Considering this background, the superior convergence characteristics of the models ROM3 and ROM4 came as a surprise. It was expected that better behaviour in this respect would come from the simplified models ROM1 and ROM2. Actually, the models ROM1 and ROM2 were intended to provide initial estimates for the models ROM3 and ROM4 but the inverse eventually
happened. A possible explanation lies in the fact that the effective diffusivities do not have, in general, the physical significance of a diffusion coefficient. The effective diffusivities may assume values ranging from minus to plus infinity. In the iterative process of solving the algebraic equations of the model even small changes in the variables can cause drastic changes in the effective diffusivities. This will affect the stability of the solution procedure introducing difficulties in reaching the solution.

The robustness of the models ROM3 and ROM4 in converging towards the solution of the problems is to be stressed as one of the greatest characteristics, if not the most important, of these reduced-order models.

12.3- CONVERGENCE OF THE SOLUTION WITH RESPECT TO THE NUMBER OF COLLOCATION POINTS EMPLOYED

A very important characteristic of the reduced-order models based on the orthogonal collocation technique presented to date in the literature lies in the rapid convergence of the solution with respect to the number of collocation points employed in the approximation. This is even more noticeable for the conditions at the ends of the column. Stewart et al. (1985) presented some data stressing this particular feature of this family of reduced-order models.

The convergence characteristics are also present in the models developed in this work, particularly those in which the interphase mass transfer rates are computed in a more rigorous way, namely, models ROM3 and ROM4. The results of the simulations confirm the conclusions of Srivastava and Joseph (1984) and Stewart et al. (1985) indicating that with five internal collocation points per section the results would be obtained with very good accuracy. This is even more noticeable at the ends of the column.

12.4- FUTURE WORK

Based on the difficulties faced during the development of this work, as well as on the acquired knowledge, some topics that deserve further research and/or
testing are presented.

The robustness of the reduced-order models ROM3 and ROM4 is to be assessed when simulating systems that involve nonideal mixtures presenting interaction effects. At the same time, the reliability of the model ROM2 (or the effective diffusivity approach based on Bird’s formulation) in predicting the interphase mass transfer rates for such systems should be addressed.

It is well known that the presence of the nonkey components in a distillation column can lead to ‘steep and flat’ composition profiles. The polynomial approximation of these profiles requires a large number of collocation points causing a low reduction on the order of the model. Furthermore, the use of polynomials of a higher degree to approximate the constant region of such profiles may introduce oscillations on the composition profiles and these oscillations would be transferred to the other profiles in the column.

Srivastava and Joseph (1987b) presented some techniques to deal with these problems in reduced-order models for tray columns. More recently Huss and Westerberg (1994) presented a technique based on variable transformations that not only tackles this problem but also alleviates the ‘bouncing of the boundary’ effect that happens when a component mole fraction approaches zero or one.

It would be extremely interesting to try incorporating the variable transformations suggested by Huss and Westerberg (1994) in the reduced-order models developed in this work.

Finally, the predictions obtained using the reduced-order models developed here should be compared with those produced using a full order nonequilibrium stage model and, what is more important, against experimental data.
### Chapter 13 - Nomenclature

#### 13- NOMENCLATURE

#### 13.1- ENGLISH LETTERS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_t$</td>
<td>cross sectional area of the column, m$^2$</td>
</tr>
<tr>
<td>$A_{i,j}^h$</td>
<td>Wassiljewa coefficient defined in equation (5.36)</td>
</tr>
<tr>
<td>$\bar{A}, \bar{B}$</td>
<td>parameters for the Soave-Redlich-Kwong equation of state</td>
</tr>
<tr>
<td>$A_{i,k}$</td>
<td>coefficients for the orthogonal collocation method</td>
</tr>
<tr>
<td>$a$</td>
<td>total interfacial area, m$^2$</td>
</tr>
<tr>
<td>$a, b$</td>
<td>parameters used to evaluate $\bar{A}$ and $\bar{B}$</td>
</tr>
<tr>
<td>$a_e$</td>
<td>effective interfacial area for mass transfer, m$^2$/m$^3$</td>
</tr>
<tr>
<td>$a_{mk}$</td>
<td>temperature dependent group interaction parameter</td>
</tr>
<tr>
<td>$a_p$</td>
<td>total surface area of the packing, m$^2$/m$^3$</td>
</tr>
<tr>
<td>$a_w$</td>
<td>wetted surface area of the packing, m$^2$/m$^3$</td>
</tr>
<tr>
<td>$\bar{a}$</td>
<td>parameter defined in equation (5.33)</td>
</tr>
<tr>
<td>$B$</td>
<td>bubble-point function</td>
</tr>
<tr>
<td>$B$</td>
<td>inverse of binary diffusion coefficient, s/m$^2$</td>
</tr>
<tr>
<td>$B$</td>
<td>structured packing channel base [see Figure 5.1], m</td>
</tr>
<tr>
<td>$B$</td>
<td>bottom product flowrate, mol/s</td>
</tr>
<tr>
<td>$B_{i,k}$</td>
<td>coefficients for the orthogonal collocation method</td>
</tr>
<tr>
<td>$[B]$</td>
<td>matrix function of inverted binary diffusion coefficients [equations (4.5) and (4.6)], s/m$^2$</td>
</tr>
<tr>
<td>$(b)$</td>
<td>column matrix of ‘intercepts’ [equation (4.51)]</td>
</tr>
<tr>
<td>$C_n$</td>
<td>coefficients in equation (5.41)</td>
</tr>
<tr>
<td>$\bar{C}_{p,i}^{*,v}$</td>
<td>ideal gas heat capacity of component $i$, J/(mol.K)</td>
</tr>
<tr>
<td>$\bar{C}_p$</td>
<td>molar heat capacity, J/(mol.K)</td>
</tr>
<tr>
<td>$\Delta \bar{C}_p$</td>
<td>residual heat capacity, J/(mol.K)</td>
</tr>
<tr>
<td>$\bar{C}_{i,1,2,...,4}$</td>
<td>constants for the evaluation of the ideal gas heat capacity</td>
</tr>
<tr>
<td>$c$</td>
<td>liquid molar volume correction factor [equation (5.11)]</td>
</tr>
<tr>
<td>$c_t$</td>
<td>mixture molar density, mol/m$^3$</td>
</tr>
<tr>
<td>$D$</td>
<td>dew-point function</td>
</tr>
</tbody>
</table>
Chapter 13 - Nomenclature

\(D\) distillate flow rate, mol/s

\([D]\) matrix of Fick diffusion coefficients, m²/s

\(L^D\) element of lower diagonal in tridiagonal matrix, mol/s

\(M^D\) element of middle diagonal in tridiagonal matrix, mol/s

\(U^D\) element of upper diagonal in tridiagonal matrix, mol/s

\(D_{ij}\) Fick diffusion coefficient for pair \(i-j\), m²/s

\(D_{i,\text{eff}}\) effective diffusivity of component \(i\) in a multicomponent mixture, m²/s

\(D_{\text{l,eff}}\) effective diffusivity of the liquid phase, m²/s

\(D_{\text{v,eff}}\) effective diffusivity of the vapour phase, m²/s

\(D_{i,j}\) Maxwell-Stefan diffusivity for pair \(i-j\), m²/s

\(D_{i,j}^\infty\) diffusion coefficient of component \(i\) infinitely diluted in component \(j\), m²/s

\(d_{eq}\) equivalent diameter of a channel [equation (5.84)], m

\(d_p\) nominal packing size or equivalent diameter of packing, m

\(d_i\) driving force for mass diffusion, m⁻¹

\(E\) energy balance function, J/s; equilibrium function

\(E\) energy flux in stationary coordinate frame of reference, J/(s.m²)

\(\xi\) total interphase energy transfer rate, J/s

\(F\) total feed rate, mol/s

\(f\) scaling parameter defined in equation (5.43)

\(f\) component feed rate, mol/s

\(f_o\) function of the acentric factor defined in equation (5.5)

\(f^{(0)}, f^{(1)}\) functions defined in equations (5.63) and (5.64)

\(f\) general function

\(f\) vector of functions

\(G\) superficial mass velocity of vapour, kg/(m².s)

\(g\) gravitational acceleration, m/s²

\(g\) vector of functions used in the homotopy methods

\(H\) heat or enthalpy balance function, J/s

\(H\) enthalpy, J/mol

\(H\) parameter defined in equation (5.42)
Chapter 13 - Nomenclature

\(H^v\)  
ideal gas enthalpy, J/mol

\(\overline{H}_i\)  
partial molar enthalpy of component \(i\), J/mol

\(H_R\)  
liquid holdup in the packing (enriching section), mol/m

\(h\)  
heat transfer coefficient, J/(s.m^2.K)

\(h\)  
scaling parameter defined in equation (5.44)

\(h\)  
structured packing crimp height [see Figure 5.1], m

\(\mathbf{h}\)  
vector of homotopy functions

\(\mathbf{h}\)  
heat transfer coefficient, m/s

\([I]\)  
identity matrix

\(J_i\)  
molar diffusion flux of component \(i\) relative to the molar average velocity, mol/(m^2 s)

\([K]\)  
diagonal matrix with the first \(n_c-1\) \(K\) values

\(K_i\)  
equilibrium ratio (\(K\) value) for component \(i\)

\(K_{OG}\)  
overall vapour phase mass transfer coefficient, mol/(m^2 s)

\([K_{ov}]\)  
matrix of multicomponent overall mass transfer coefficients, m/s

\(k\)  
mass transfer coefficient in a binary mixture, m/s

\([k]\)  
matrix of multicomponent mass transfer coefficients, m/s

\(k_{i,eff}\)  
effective (pseudobinary) mass transfer coefficient of component \(i\) in a multicomponent mixture, m/s

\(\overline{k}_{ij}\)  
binary interaction parameter [equations (5.6), (5.17), and (5.31)]

\(L\)  
total liquid flow, mol/s

\(\overline{L}\)  
total liquid flow in the stripping section, mol/s

\(\overline{L}\)  
superficial mass velocity of liquid, kg/(m^2 s)

\(Le\)  
Lewis number

\(l\)  
component liquid flow, mol/s

\(\ell\)  
generalised characteristic length, m

\(M\)  
mass balance function, mol/s

\(\mathbf{M}\)  
liquid holdup, mol

\(\tilde{M}\)  
liquid holdup per unit height of the column, mol/m

\(\mathbf{M}\)  
molecular weight, kg/mol
Chapter 13 - Nomenclature

$[M]$ matrix of equilibrium constants

$M_{av}$ average molecular weight defined in equation (5.58), kg/mol

$m$ number of internal collocation points used in the approximation

$N_S$ number of equilibrium-stages in the column

$N_T$ number of trays or sections of packing in the column

$N_i$ molar flux of component $i$ referred to a stationary coordinate reference frame, mol/(m$^2$s)

$N_t$ total molar flux referred to a stationary coordinate reference frame, mol/(m$^2$s)

$N_i$ molar flux of component $i$ referred to a stationary coordinate reference frame, mol/(m$^2$s)

$N_t$ mixture molar flux referred to a stationary coordinate reference frame, mol/(m$^2$s)

$\mathcal{N}$ total interphase mass transfer rate, mol/(s.m)

$\mathcal{N}_i$ total interphase mass transfer rate, mol/s

$n$ number of internal collocation points used in the approximation

$n$ number of lumped trays in a nonequilibrium method

$n_k$ total number of groups ($k$) in the mixture

$nc$ number of components

$P$ pressure, Pa

$P_c$ critical pressure, Pa

$P_k^s$ vapour pressure of component $k$, Pa

$\{P\}$ parachor [see equation (5.21)]

$p$ number of variables or equations on the Newton-Raphson method

$p_i$ partial pressure of component $i$, Pa

$Q$ heat removal from the stage, J/s

$Q^l$ heat removal from liquid phase, J/s

$Q^v$ heat removal from vapour phase, J/s

$Q_k$ surface area parameter for group $k$

$Q_{ij}$ interface equilibrium function

$q$ convective heat transfer rate, J/(s.m)

$q$ conductive heat flux, J/(s.m$^2$)
Chapter 13 - Nomenclature

$q$ conductive heat transfer rate, J/(s.m)

$R$ rate function, mol/s or mol/(s.m) or mol/m$^2$

$R$ gas constant, 8.314 J/(mol.K)

$[R]$ matrix function of inverted binary mass transfer coefficients [equations (4.62) and (4.63)], s/m

$R_R$ reflux ratio

$R_k$ volume parameter for group $k$

$r$ ratio of side stream to interstage flow

$r_i$ molecular volume parameter for component $i$ [equation (5.70)]

$S$ mole fraction summation function

$S$ structured packing channel side [see Figure 5.1], m

$S$ side stream flowrate, mol/s

$T$ temperature, K

$T_c$ critical temperature, K

$T_b$ normal boiling point, K

$T_r$ reduced temperature, $T/T_c$

$T^*$ reduced temperature parameter defined in equation (5.45)

$T_{SC}$ degrees of subcooling of the reflux, K

$t$ time, s

$t_h$ homotopy parameter

$U$ element of the vector of feeds' specifications, mol/s

$u$ superficial velocity [equations (5.82) and (5.86)], m/s

$u_{eff}$ effective velocity [equations (5.80) and (5.85)], m/s

$V$ total vapour flow, mol/s

$\bar{V}$ total vapour flow in the stripping section, mol/s

$V_c$ critical volume, cm$^3$/mol

$\bar{V}$ molar volume, m$^3$/mol

$\hat{V}$ molar volume at the normal boiling point, m$^3$/mol

$v$ component vapour flow, mol/s

$w_i$ modified volume fraction of component $i$ in the mixture [equation (5.67)]

$x$ liquid phase mole fraction
Chapter 13 - Nomenclature

$x$ general variable
$x$ vector of variables
$y$ vapour phase mole fraction
$y_k$ vapour mole fraction in equilibrium with a liquid with mole fraction $x_k$
$Z_p$ packed height, m
$Z_R$ height of packing in the rectification section of the column, m
$Z_S$ height of packing in the stripping section of the column, m
$z$ feed mole fraction
$z$ coordinate direction or position, m
$z$ compressibility factor
$z$ lattice coordination number
$z_c$ critical compressibility factor
$Z_{RA}$ Rackett compressibility factor
$Z_{Rh}, Z_S$ spatial variables, m
$Z_{R}, Z_S$ dimensionless spatial variables

13.2- Greek Letters

$\alpha$ relative volatility
$\alpha$ parameter defined in equations (5.54) and (5.55)
$\alpha$ association factor of solvent [equation (5.59)]
$[\beta]$ bootstrap matrix
$\chi$ variable defined in equation (3.35)
$\delta$ distance from the interface, m
$\delta_{ij}$ Kronecker delta, 1 if $i = k$ and 0 otherwise
$\varepsilon$ void fraction of the packing
$\Phi$ mass transfer rate factor for explicit methods
$\Phi_{\text{eff}}$ mass transfer rate factor in effective diffusivity (pseudobinary) methods
$\Phi_H$ heat transfer rate factor
$[\Phi]$ matrix of mass transfer rate factors
$\phi_i$ superficial volume fraction of component $i$ [equation (5.48)]
Chapter 13 - Nomenclature

(\phi) column matrix of dimensionless mass transfer parameters

\Gamma thermodynamic factor for a binary system

\Gamma reduced, inverse thermal conductivity [equation (5.38)], s.m.K/J

\Gamma_k activity coefficient of group k at mixture composition [equation (5.69)]

\Gamma'_k activity coefficient of group k at a group composition corresponding to
pure component i [equation (5.69)]

[\Gamma] matrix of thermodynamic factors (equation 4.9)

[\Gamma] matrix of thermodynamic factors (equation 4.119)

\gamma_i activity coefficient of component i in solution

\gamma^c_i combinatorial part of the activity coefficient, equation (5.66)

\gamma'_i residual part of the activity coefficient, equation (5.68)

\gamma activity coefficient

\eta dimensionless distance

\eta viscosity, kg/(m.s)

\eta^* viscosity parameter defined in equation (5.40)

\eta_0 viscosity parameter defined in equation (5.41)

\psi variable defined in equation (3.34)

K_O parameter in equation (5.75)

K_S parameter in equation (3.74)

\kappa_{ij} Maxwell-Stefan mass transfer coefficient for the binary pair i-j, m/s

\kappa^V_eff effective mass transfer coefficient of the vapour phase, m/s

\kappa^L_eff effective mass transfer coefficient of the liquid phase, m/s

\Lambda dimensionless parameters

\Lambda liquid flow per unit length perimeter [equation (5.81)], kg/(m^3.s)

\lambda thermal conductivity, J/(s.m.K)

\lambda_{i,j} average thermal conductivity defined in equation (5.47), J/(s.m.K)

\lambda_{tr} monatomic thermal conductivity [equation (5.37)], J/(s.m.K)

\mu_i molar chemical potential of component i, J/mol

\nu_i determinacy coefficient for component i, various units

\tilde{\nu} mole fraction weighted sum of component determinacy coefficients
Chapter 13 - Nomenclature

\( v_k' \) number of groups \( k \) present in molecule \( i \) [equation (5.68)]

\( \Pi \) general property, various units

\( \pi \) constant, 3.14159...

\( [\Theta] \) matrix of rate factors in approximate methods for nonideal systems

\( \theta \) angle of flow channel [see Figure 5.1], degrees

\( \theta_k \) surface area fraction for \( k \) in the mixture [equation (5.71)]

\( \rho \) density, kg/m\(^3\)

\( \rho_c \) critical density, kg/m\(^3\)

\( \rho_r \) reduced density defined in equation (5.56)

\( \Sigma_Y \) Fuller et al. parameter [equation (5.57)]

\( \sigma \) surface tension, N/m

\( \sigma_c \) critical surface tension of the packing material, N/m

\( \tau_{ij} \) Boltzmann factors [equation (5.72)]

\( [Y] \) matrix of mass transfer rate factors in the exact solution for nonideal fluid systems

\( [\Omega_0'(A)] \) matrizont of matrix \( [A] \) according to definition in equation (4.96)

\( \omega \) Pitzer's acentric factor

\( \Xi \) correction factor for high fluxes in binary mass transfer; correction factor for high fluxes in explicit methods; general multiplier defined in equation (2.18)

\( [\Xi] \) matrix of high flux correction factors

\( \Xi_{i,\text{eff}} \) correction factor for high fluxes in effective diffusivity (pseudobinary) methods

\( \Xi_H \) correction factor for the effect of high fluxes on the heat transfer coefficient

\( [\Psi] \) matrix of mass transfer rate factors in the linearised film model

\( [\Psi] \) matrix defined by equations (4.115) and (4.116)

13.3- Subscripts

\( A \) referring to component \( A \)
indicates that averaged properties are employed in the evaluation of
the indicated parameter
referring to component B; referring to the bottom of the column
referring to the bottom of the rectification section
referring to the bottom of the stripping section
referring to the bubble point
bulk phase property
calculated value
corrected value
referring to the distillate
referring to the feed
referring to the interface
referring to component i
referring to component j; referring to stage j; referring to collocation
point j
referring to component k; referring to collocation point k; referring to
stage number k; referring to iteration number k
referring to the liquid phase
referring to the mixture
denotes reference quantity; referring to the rectification section
denotes a reduced property
referring to the stripping section
referring to the top of the rectification section
referring to the top of the stripping section
referring to the vapour-gas phase
quantity evaluated at position \( \eta = \delta \)
quantity evaluated at position \( \eta = 0 \)

13.4- Superscripts
referring to the total feed
referring to the interface
referring to the liquid phase
Chapter 13 - Nomenclature

\[ LF \quad \text{liquid feed} \]
\[ O \quad \text{referring to an overall balance} \]
\[ V \quad \text{referring to the vapour-gas phase} \]
\[ VF \quad \text{vapour feed} \]
\[ ^\wedge \quad \text{Eigenvalue of corresponding matrix} \]
\[ \cdot \quad \text{partial property; average bulk phase condition} \]
\[ ' \quad \text{first derivative} \]
\[ * \quad \text{referring to finite transfer rates} \]

13.5- **MATHEMATICAL SYMBOLS AND MATRIX NOTATION**

\[ \nabla \quad \text{gradient} \]
\[ \Delta \quad \text{difference operator} \]
\[ \lim \quad \text{limit} \]
\[ ( ) \quad \text{column matrix} \]
\[ [ ] \quad \text{square matrix} \]
\[ [ ]^{-1} \quad \text{inverse of a square matrix} \]
\[ ( )^T \quad \text{transpose of a column matrix} \]
Chapter 14 - References

14- REFERENCES


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APPENDIX 1 - POLYNOMIALS EMPLOYED IN THE SIMULATIONS

The polynomials employed in the simulations were Jacobi polynomials defined by the following equation:

\[ \int_0^1 P_k(x)P_m(x)dx = 0 \quad k = 0, 1, 2, \ldots, m - 1 \]  \hspace{1cm} (A1.1)

with the first coefficient taken as equal to one.

The collocation points are the roots of these polynomials. For a given number of internal collocation points, \( m \), the roots \( x_2, \ldots, x_{m+1} \) are given below; \( x_1 = 0 \) and \( x_{m+2} = 1.0 \).

<table>
<thead>
<tr>
<th>( m )</th>
<th>( x_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.211324865 0.788675135</td>
</tr>
<tr>
<td>3</td>
<td>0.112701665 0.500000000 0.887298335</td>
</tr>
<tr>
<td>4</td>
<td>0.069431844 0.330009478 0.669990522 0.930568156</td>
</tr>
<tr>
<td>6</td>
<td>0.033765243 0.169395307 0.380690407 0.619309593 0.830604693 0.966234757</td>
</tr>
<tr>
<td>10</td>
<td>0.013046736 0.067468317 0.160295216 0.283302303 0.425562831 0.574437169 0.716697697 0.839704784 0.932531683 0.986953264</td>
</tr>
</tbody>
</table>
APPENDIX 2 - SIMPLIFIED FLOWCHART FOR THE REDUCED-ORDER MODELS

A simplified flowchart for the reduced-order models developed in this work is presented in Figure A2.1. The reduced-order model ROM1 uses the part of the flowchart drawn in black. The models ROM2 and ROM3 are represented by the combination of the flowcharts drawn in black and in blue. Finally, the model ROM4 uses the complete flowchart.

For the property evaluation section the models share the subroutines without any changes. The only exception is subroutine MASSTRAN that will be different for every model because different procedures are used in the evaluation of the interphase mass transfer rates.

A brief description of the subroutines is given below:

**Main program:** the main program reads all the data from a file and after storing them in the appropriate vectors and matrices calls subroutine LMODIN. Subroutine LMODIN is responsible for the initialisation needed for the computation of the activity coefficients. After the return to the main program subroutine IMPRIM will be called.

**Subroutine IMPRIM:** initially the size of the matrices and vectors is adjusted according to the number of collocation points employed in the approximation and the number of components in the mixture. The solution of the system of algebraic equations is sought using subroutine C05NDF. There is a strong interaction between subroutines IMPRIM and C05NDF. Depending on the output from C05NDF the subroutine IMPRIM will either print intermediate values for the variables, print the converged values of the variables, or call subroutine FCN for the evaluation of the functions for the current values of the variables. When the system of equations is converged subroutine IMPRIM sends the results to an output file.

**Subroutine FCN:** is responsible for evaluating the functions for a given set of values of the variables.

**Subroutine MINV:** calculates the inverse of a matrix. It is called by subroutine
Figure A2.1. Simplified flowchart for the reduced-order models
MASSTRAN (only for the model ROM4) to compute the inverse of the matrix of thermodynamic factors. This matrix inversion is needed in the computation of the matrix of mass transfer rate factors using equation (4.114).

**Subroutine C05NDF**: subroutine used for the solution of the system of nonlinear algebraic equations of the reduced-order models. Its algorithm is based in a modification of Powell's hybrid method [Powell (1970)]. C05NBF is a subroutine from the NAG FORTRAN Workstation Library, produced by The Numerical Algorithm Group Ltd.

**Subroutine F02AFF**: subroutine used for the computation of the eigenvalues of a matrix. It is used in model ROM4 for the evaluation of the eigenvalues of the matrix of mass transfer rate factors. Subroutine F02AFF is from the same library of subroutines quoted above.

The remaining subroutines are used in the evaluation of several properties of the system needed in the simulations. A description of the methods used in each of these subroutines can be found in chapter five.
APPENDIX 3 - CPU TIME SPENT IN THE SIMULATIONS

In order to allow some further comparison between the performance of the different reduced-order models one will find in Tables A3.1 to A3.3 the CPU time spent in the simulations of the three case studies.

**Table A3.1. CPU time (s) spent in the simulations of case study 1**

<table>
<thead>
<tr>
<th>n and m</th>
<th>ROM4</th>
<th>ROM3</th>
<th>ROM2</th>
<th>ROM1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>57.4</td>
<td>53.2</td>
<td>51.6</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>57.0</td>
<td>51.2</td>
<td>87.1</td>
<td>-------</td>
</tr>
<tr>
<td>4</td>
<td>67.6</td>
<td>61.0</td>
<td>61.5</td>
<td>0.8</td>
</tr>
<tr>
<td>6</td>
<td>227.0</td>
<td>203.4</td>
<td>105.9</td>
<td>1.3</td>
</tr>
<tr>
<td>10</td>
<td>514.8</td>
<td>474.1</td>
<td>237.6</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The codes appearing in the tables have the following meaning:

1. extra evaluations of the Jacobian were needed in order to reach the solution of the problem;
2. there was no convergence on the values of the overall mass transfer coefficient (entry specific for the model ROM1);
3. solution obtained using the results from the simulation with the model...
ROM3 as the guesses to start the iterative procedure;

failed; it was not possible to find the solution of the problem using this model.

**Table A3.3. CPU time (s) spent in the simulations of case study 3**

<table>
<thead>
<tr>
<th>n and m</th>
<th>ROM4</th>
<th>ROM3</th>
<th>ROM2</th>
<th>ROM1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>54.0</td>
<td>48.8</td>
<td>27.5</td>
<td>------</td>
</tr>
<tr>
<td>3</td>
<td>45.4</td>
<td>40.9</td>
<td>45.4</td>
<td>------</td>
</tr>
<tr>
<td>4</td>
<td>64.4</td>
<td>58.5</td>
<td>109.7</td>
<td>------</td>
</tr>
<tr>
<td>6</td>
<td>113.1</td>
<td>103.1</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>10</td>
<td>258.9</td>
<td>234.7</td>
<td>------</td>
<td>------</td>
</tr>
</tbody>
</table>

It is important to stress that the values presented in these tables are approximated values. The simulations were performed on a IBM RS/6000 550 (o/s IBM AIX 3.2.5; real memory 128 Mb; swap space 408 Mb; 41.7 Mhz clock; 64 Kb data cache; 8 Kb instruction cache; 23.0 Mflops; and 54.3 SPEC marks) on a 'time sharing' basis. Therefore depending on how busy the system was at the moment of the simulations the input (output) of data from (to) the files would take longer. Furthermore, the values presented for the model ROM1 can be misleading as they include only the time spent in the 'last iteration' of the procedure to converge the values of the overall mass transfer coefficients. This convergence was made off-line, feeding the results from the simulation with ROM1 to a program to calculate the overall mass transfer coefficients and these new values were feed back into ROM1.

It is also noteworthy that, at this stage, there was no concern in trying to optimise the CPU time spent in the simulations. These times can be improved by using specially tailored subroutines for the solution of the system of algebraic equations of the models.

It is clear from the values presented in the tables that, except on case study 1
where there was a similarity in the performance of the models ROM2, ROM3, and ROM4, models ROM3 and ROM4 outperformed model ROM2.

One can also see that the computation of the high flux correction factors (in model ROM4) increased the time spent in the simulations without such corrections (in model ROM3) by approximately ten percent.