Chapter 2

Distillation Theory

by

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This is a revised version of an article accepted for publication in the Encyclopedia of Separation Science by Academic Press Ltd. (submitted in 1999). *This article gives some of the basics of distillation theory and its purpose is to provide basic understanding and some tools for simple hand calculations of distillation columns. The methods presented here can be used for simple estimates and to check more rigorous computations.*

2.1 Introduction

Distillation is a very old separation technology for separating liquid mixtures that can be traced back to the chemists in Alexandria in the first century A.D. Today distillation is the most important industrial separation technology. It is particularly well suited for high purity separations since any degree of separation can be obtained with a fixed energy consumption by increasing the number of equilibrium stages.

To describe the degree of separation between two components in a column or in a column section, we introduce the separation factor:

$$S = \frac{(x_L/x_H)_T}{(x_L/x_H)_B} \tag{2.1}$$

where here x denotes mole fraction of a component, subscript L denotes light component, H heavy component, T denotes the top of the section, and B the bottom.

It is relatively straightforward to derive models of distillation columns based on almost any degree of detail, and also to use such models to simulate the behaviour on a computer. However, such simulations may be time consuming and often provide limited insight. The objective of this article is to provide analytical expressions that are useful for understanding the fundamentals of distillation and which may be used to guide and check more detailed simulations:

- Minimum energy requirement and corresponding internal flow requirements.
- Minimum number of stages.
- Simple expressions for the separation factor.

The derivation of analytical expressions requires the assumptions of:

- Equilibrium stages.
- Constant relative volatility.
- Constant molar flows.

These assumptions may seem restrictive, but they are actually satisfied for many real systems, and in any case the resulting expressions yield invalueable insights, also for systems where the approximations do not hold.

2.2 Fundamentals

2.2.1 The Equilibrium Stage Concept

The equilibrium (theoretical) stage concept (see Figure 2.1) is central in distillation. Here we assume vapour-liquid equilibrium (VLE) on each stage and that the liquid is sent to the stage below and the vapour to the stage above. For some trayed columns this may be a reasonable description of the actual physics, but it is certainly not for a packed column. Nevertheless, it is established that calculations based on the equilibrium stage concept (with the number of stages adjusted appropriately) fits data from most real columns very well, even packed columns.

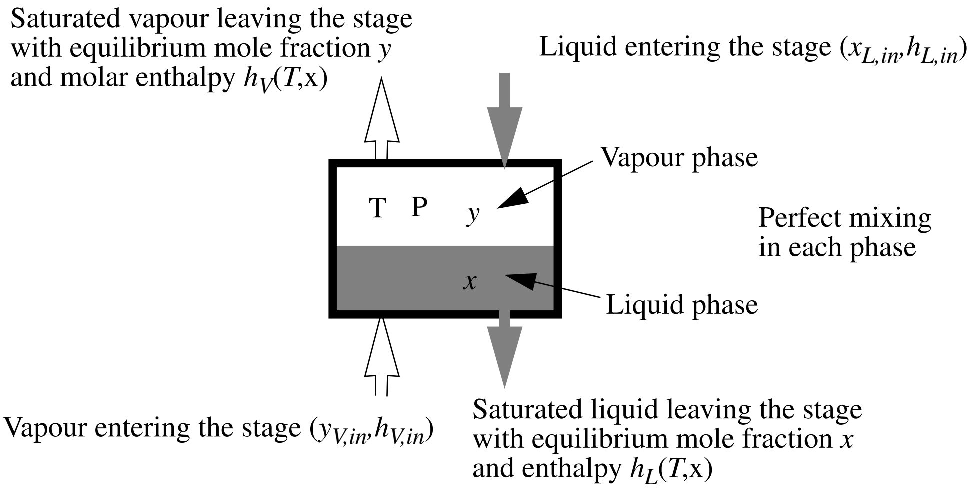

Figure 2.1: Equilibrium stage concept.

One may refine the equilibrium stage concept, e.g. by introducing back mixing or a Murphee efficiency factor for the equilibrium, but these “fixes” have often relatively little theoretical justification, and are not used in this article.

For practical calculations, the critical step is usually not the modelling of the stages, but to obtain a good description of the VLE. In this area there has been significant advances in the last 25 years, especially after the introduction of equations of state for VLE prediction. However, here we will use simpler VLE models (constant relative volatility) which apply to relatively ideal mixtures.

2.2.2 Vapour-Liquid Equilibrium (VLE)

In a two-phase system (PH=2) with N_c non-reacting components, the state is completely determined by N_c degrees of freedom (f), according to Gibb’s phase rule;

$$f = N_c + 2 - PH \tag{2.2}$$

If the pressure (P) and N_c-1 liquid compositions or mole fractions (x) are used as degrees of freedom, then the mole fractions (y) in the vapour phase and the temperature (T) are determined, provided that two phases are present. The general VLE relation can then be written:

$$\begin{aligned} [y_1, y_2, \ldots, y_{N_c-1}, T] &= f(P, x_1, x_2, \ldots, x_{N_c-1}) \\ [y, T] &= f(P, x) \end{aligned} \tag{2.3}$$

Here we have introduced the mole fractions x and y in the liquid an vapour phases respectively, and we trivially have $\sum_{i=1}^{n} x_i = 1$ and $\sum_{i=1}^{n} y_i = 1$

In ideal mixtures, the vapour liquid equilibrium can be derived from Raoult's law which states that the partial pressure p_i of a component (i) in the vapour phase is proportional to the vapour pressure (p_i^o) of the pure component (which is a function of temperature only: $p_i^o = p_i^o(T)$) and the liquid mole fraction (x_i):

$$p_i = x_i p_i^o(T) \tag{2.4}$$

For an ideas gas, according to Dalton's law, the partial pressure of a component is proportional to the mole fraction: $p_i = y_i P$, and since the total pressure $P = p_1 + p_2 + \ldots + p_{N_c} = \sum_i p_i = \sum_i x_i p_i^o(T)$ we derive:

$$y_i = x_i \frac{p_i^o}{P} = \frac{x_i p_i^o(T)}{\sum_i x_i p_i^o(T)} \tag{2.5}$$

The following empirical formula is frequently used for computing the pure component vapour pressure:

$$\ln p^o(T) \approx a + \frac{b}{c+T} + d\ln(T) + eT^f \tag{2.6}$$

The coefficients are listed in component property data bases. The case with d=e=0 is called the Antoine equation.

2.2.3 K-values and Relative Volatility

The K-value for a component i is defined as: $K_i = y_i / x_i$. The K-value is sometimes called the equilibrium "constant", but this is misleading as it depends strongly on temperature and pressure (or composition).

The relative volatility between components i and j is defined as:

$$\alpha_{ij} = \frac{(y_i/x_i)}{(y_j/x_j)} = \frac{K_i}{K_j} \tag{2.7}$$

For ideal mixtures that satisfy Raoult's law we have:

$$\alpha_{ij} = \frac{(y_i/x_i)}{(y_j/x_j)} = \frac{K_i}{K_j} = \frac{p_i^o(T)}{p_j^o(T)} \tag{2.8}$$

Here $p_i^o(T)$ depends on temperature so the K-values will actually be constant only close to the column ends where the temperature is relatively constant. On the other hand the ratio $p_i^o(T)/p_j^o(T)$ is much less dependent on temperature which makes the relative volatility very attractive for computations. For ideal mixtures, a geometric average of the relative volatilities for the highest and lowest temperature in the column usually gives sufficient accuracy in the computations: $\alpha_{ij} = \sqrt{\alpha_{ij,\,top} \cdot \alpha_{ij,\,bottom}}$.

We usually select a common reference component r (usually the least volatile (or "heavy") component), and define:

$$\alpha_i = \alpha_{ir} = p_i^o(T)/p_r^o(T) \tag{2.9}$$

The VLE relationship (2.5) then becomes:

$$y_i = \frac{\alpha_i x_i}{\sum_i \alpha_i x_i} \tag{2.10}$$

For a binary mixture we usually omit the component index for the light component, i.e. we write $x=x_1$ (light component) and $x_2=1-x$ (heavy component). Then the VLE relationship becomes:

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \tag{2.11}$$

This equilibrium curve is illustrated in Figure 2.2:

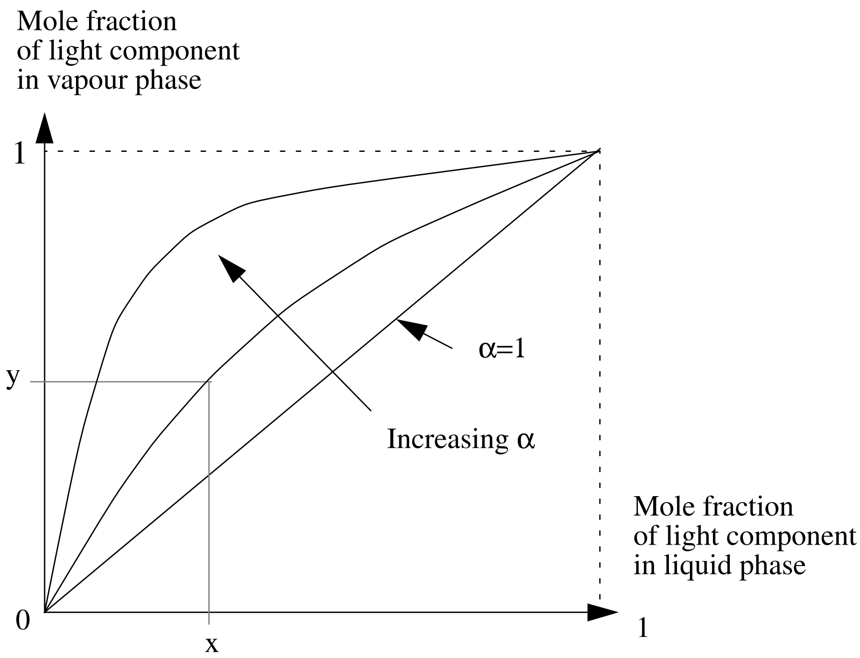

Figure 2.2: VLE for ideal binary mixture: $y = \frac{\alpha x}{1 + (\alpha - 1)x}$

The difference y-x determine the amount of separation that can be achieved on a stage. Large relative volatilities implies large differences in boiling points and easy separation. Close boiling points implies relative volatility closer to unity, as shown below quantitatively.

2.2.4 Estimating the Relative Volatility From Boiling Point Data

The Clapeyron equation relates the vapour pressure temperature dependency to the specific heat of vaporization (ΔH^{vap}) and volume change between liquid and vapour phase (ΔV^{vap}):

$$\frac{dp^o(T)}{dT} = \frac{\Delta H^{vap}(T)}{T\Delta V^{vap}(T)} \tag{2.12}$$

If we assume an ideal gas phase, and that the gas volume is much larger than the liquid volume, then $\Delta V^{vap} \approx RT/P$, and integration of Clapeyrons equation from temperature T_{bi} (boiling point at pressure P_{ref}) to temperature T (at pressure p_i^o) gives, when ΔH_i^{vap} is assumed constant:

$$\ln p_i^o \approx \left(\frac{\Delta H_i^{vap}}{R}\left(\frac{1}{T_{bi}}\right) + \ln P_{ref}\right) + \frac{\left(-\frac{\Delta H_i^{vap}}{R}\right)}{T} \tag{2.13}$$

This gives us the Antoine coefficients:

$$a_i = \frac{\Delta H_i^{vap}}{R}\left(\frac{1}{T_{bi}}\right) + \ln P_{ref},\ b_i = -\frac{\Delta H_i^{vap}}{R},\ c_i = 0\ .$$

In most cases $P_{ref} = 1\ atm$. For an ideal mixture that satisfies Raoult's law we have $\alpha_{ij} = p_i^o(T)/p_j^o(T)$ and we derive:

$$\ln\alpha_{ij} = \frac{\Delta H_i^{vap}}{R}\frac{1}{T_{bi}} - \frac{\Delta H_j^{vap}}{R}\frac{1}{T_{bj}} + \frac{\Delta H_j^{vap} - \Delta H_i^{vap}}{RT} \tag{2.14}$$

We see that the temperature dependency of the relative volatility arises from different specific heat of vaporization. For similar values ($\Delta H_i^{vap} \approx \Delta H_j^{vap}$), the expression simplifies to:

$$\ln\alpha_{ij} \approx \underbrace{\frac{\Delta\overline{H}^{vap}}{R\overline{T}_b}}_{\beta}\frac{T_{bj} - T_{bi}}{\overline{T}_b} \qquad where\ \overline{T}_b = \sqrt{T_{bi}T_{bj}} \tag{2.15}$$

Here we may use the geometric average also for the heat of vaporization:

$$\Delta\overline{H}^{vap} = \sqrt{\Delta H_i^{vap}(T_{bi}) \cdot \Delta H_j^{vap}(T_{bj})} \tag{2.16}$$

This results in a rough estimate of the relative volatility α_{ij}, based on the boiling points only:

$$\alpha_{ij} \approx e^{\beta(T_{bj} - T_{bi})/T_b} \text{ where } \beta = \frac{\Delta \bar{H}^{vap}}{R \bar{T}_B} \tag{2.17}$$

If we do not know $\Delta \bar{H}^{vap}$, a typical value $\beta \approx 13$ can be used for many cases.

> Example: *For methanol (L) and n-propanol (H), we have* $T_{BL} = 337.8K$ *and* $T_{BH} = 370.4K$ *and the heats of vaporization at their boiling points are 35.3 kJ/mol and 41.8 kJ/mol respectively. Thus*
> $\bar{T}_B = \sqrt{337.8 \cdot 370.4} = 354K$ *and* $\Delta \bar{H}^{vap} = \sqrt{35.3 \cdot 41.8} = 38.4$.
> *This gives* $\beta = \Delta \bar{H}^{vap} / R \bar{T}_B = 38.4/(8.83 \cdot 354) = 13.1$ *and*
> $\alpha \approx e^{13.1 \cdot 32.6/354} \approx 3.34$ *which is a bit lower than the experimental value.*

2.2.5 Material Balance on a Distillation Stage

Based on the equilibrium stage concept, a distillation column section is modelled as shown in Figure 2.3: Note that we choose to number the stages starting from the bottom of the column. We denote L_n and V_n as the total liquid- and vapour molar flow rates leaving stage *n* (and entering stages *n-1* and *n+1*, respectively).

We assume perfect mixing in both phases inside a stage. The mole fraction of species i in the vapour leaving the stage with V_n is $y_{i,n}$, and the mole fraction in L_n is $x_{i,n}$.

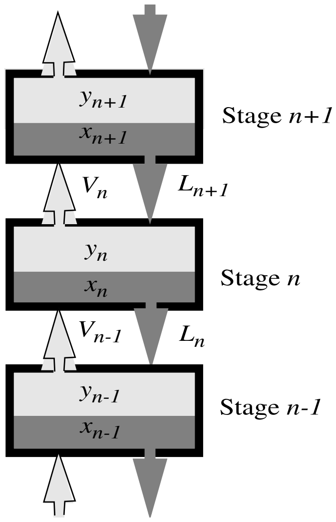

Figure 2.3: Distillation column section modelled as a set of connected equilibrium stages

The material balance for component i at stage n then becomes (in [*mol i/sec*]):

$$\frac{dN_{i,n}}{dt} = (L_{n+1}x_{i,n+1} - V_n y_{i,n}) - (L_n x_{i,n} - V_{n-1} y_{i,n-1}) \tag{2.18}$$

where $N_{i,n}$ in the number of moles of component i on stage n. In the following we will consider steady state operation, i.e: $\frac{dN_{i,n}}{dt} = 0$.

It is convenient to define the net material flow (w_i) of component i upwards from stage n to $n+1$ [*mol i/sec*]:

$$w_{i,n} = V_n y_{i,n} - L_{n+1} x_{i,n+1} \tag{2.19}$$

At steady state, this net flow has to be the same through all stages in a column section, i.e. $w_{i,n} = w_{i,n+1} = w_i$.

The material flow equation is usually rewritten to relate the vapour composition (y_n) on one stage to the liquid composition on the stage above (x_{n+1}):

$$y_{i,n} = \frac{L_{n+1}}{V_n} x_{i,n+1} + \frac{1}{V_n} w_i \tag{2.20}$$

The resulting curve is known as the operating line. Combined with the VLE relationship (equilibrium line) this enables us to compute all the stage compositions when we know the flows in the system. This is illustrated in Figure 2.4, and forms the basis of the McCabe-Thiele approach.

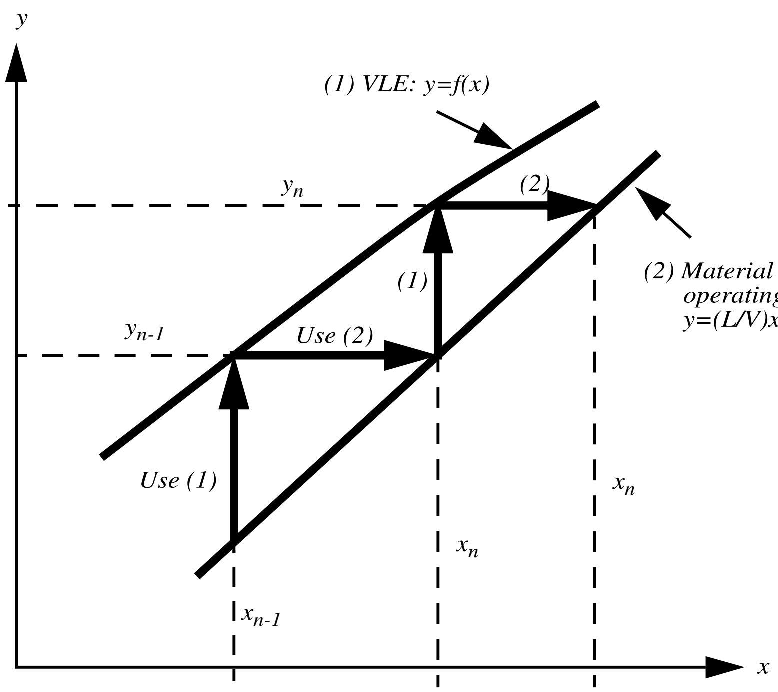

Figure 2.4: Combining the VLE and the operating line to compute mole fractions in a section of equilibrium stages.

2.2.6 Assumption about Constant Molar Flows

In a column section, we may very often use the assumption about constant molar flows. That is, we assume $L_n = L_{n+1} = L$ [*mol/s*] and $V_{n-1} = V_n = V$ [*mol/s*]. This assumption is reasonable for ideal mixtures when the components have similar molar heat of vaporization. An important implication is that the operating line is then a straight line for a given section, i.e $y_{i,n} = (L/V)x_{i,n+1} + w_i/V$. This makes computations much simpler since the internal flows (L and V) do not depend on compositions.

2.3 The Continuous Distillation Column

We here study the simple two-product continuous distillation column in Figure 2.5: We will first limit ourselves to a binary feed mixture, and the component index is omitted, so the mole fractions (x,y,z) we refer to the light component. The column has N equilibrium stages, with the reboiler as stage number 1. The feed with total molar flow rate F [*mol/sec*] and mole fraction z enters at stage N_F.

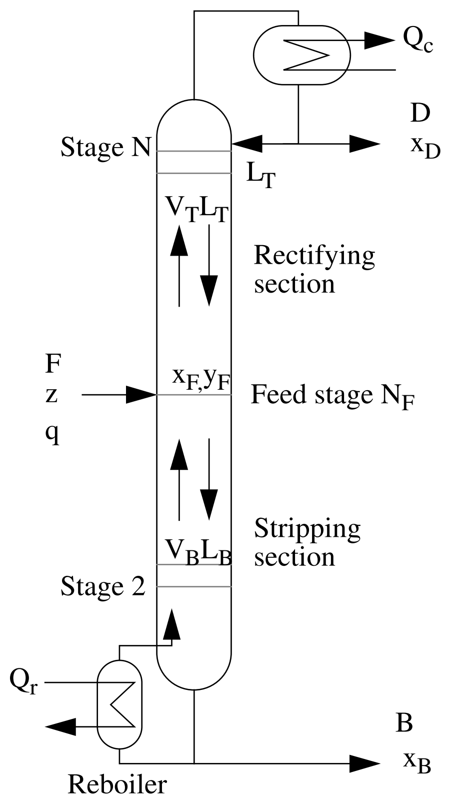

Figure 2.5: An ordinary continuous two-product distillation column

The section above the feed stage is denoted the rectifying section, or just the top section, and the most volatile component is enriched upwards towards the distillate product outlet (D). The stripping section, or the bottom section, is below the feed, in which the least volatile component is enriched towards the bottoms product outlet (B). (The least volatile component is "stripped" out.) Heat is supplied in the reboiler and removed in the condenser, and we do not consider any heat loss along the column.

The feed liquid fraction q describes the change in liquid and vapour flow rates at the feed stage:

$$\begin{aligned} \Delta L_F &= qF \\ \Delta V_F &= (1-q)F \end{aligned} \tag{2.21}$$

The liquid fraction is related to the feed enthalpy (h_F) as follows:

$$q = \frac{h_{V,sat} - h_F}{\Delta H^{vap}} = \begin{cases} > 1 & \textit{Subcooled liquid} \\ = 1 & \textit{Saturated liquid} \\ 0 < q < 1 & \textit{Liquid and vapour} \\ = 0 & \textit{Saturated vapour} \\ < 0 & \textit{Superheated vapour} \end{cases} \tag{2.22}$$

When we assume constant molar flows in each section, we get the following relationships for the flows:

$$\begin{aligned} V_T &= V_B + (1-q)F \\ L_B &= L_T + qF \\ D &= V_T - L_T \\ B &= L_B - V_B \end{aligned} \tag{2.23}$$

2.3.1 Degrees of Freedom in Operation of a Distillation Column

With a given feed (F,z and q), and column pressure (P), we have only 2 degrees of freedom in operation of the two-product column in Figure 2.5, independent of the number of components in the feed. This may be a bit confusing if we think about degrees of freedom as in Gibb's phase rule, but in this context Gibb's rule does not apply since it relates the thermodynamic degrees of freedom inside a single equilibrium stage.

This implies that if we know, for example, the reflux (L_T) and vapour (V_B) flow rate into the column, all states on all stages and in both products are completely determined.

2.3.2 External and Internal Flows

The overall mass balance and component mass balance is given by:

$$\begin{aligned} F &= D + B \\ Fz &= Dx_D + Bx_B \end{aligned} \tag{2.24}$$

Here z is the mole fraction of light component in the feed, and x_D and x_B are the product compositions. For sharp splits with $x_D \approx 1$ and $x_B \approx 0$ we then have that $D=zF$. In words, we must adjust the product split *D/F* such that the distillate flow equals the amount of light component in the feed. Any deviation from this value will result in large changes in product composition. This is a very important insight for practical operation.

> Example: *Consider a column with z=0.5, x_D=0.99, x_B=0.01 (all these refer to the mole fraction of light component) and D/F = B/F = 0.5. To simplify the discussion set F=1 [mol/sec]. Now consider a 20% increase in the distillate D from 0.50 to 0.6 [mol/sec]. This will have a drastic effect on composition. Since the total amount of light component available in the feed is z = 0.5 [mol/sec], at least 0.1 [mol/sec] of the distillate must now be heavy component, so the amount mole fraction of light component in the distillate is now at its best 0.5/0.6 = 0.833. In other words, the amount of heavy component in the distillate will increase at least by a factor of 16.7 (from 1% to 16.7%).*

Thus, we generally have that a change in *external flows* (D/F and B/F) has a large effect on composition, at least for sharp splits, because any significant deviation in D/F from z implies large changes in composition. On the other hand, the effect of changes in the *internal flows* (L and V) are much smaller.

2.3.3 McCabe-Thiele Diagram (Constant Molar Flows, but any VLE)

The McCabe-Thiele diagram where y is plotted as a function x along the column provides an insightful graphical solution to the combined mass balance (“operation line”) and VLE (“equilibrium line”) equations. It is mainly used for binary mixtures. It is often used to find the number of theoretical stages for mixtures with constant molar flows. The equilibrium relationship $y_n = f(x_n)$ (y as a function of x at the stages) may be nonideal. With constant molar flow, L and V are constant within each section and the operating lines (y as a function of x between the stages) are straight. In the top section the net transport of light component $w = x_D D$. Inserted into the material balance equation (2.20) we obtain the operating line for the top section, and we have a similar expression for the bottom section:

$$\begin{aligned} \textit{Top:} \quad & y_n = \left(\frac{L}{V}\right)_T (x_{n+1} - x_D) + x_D \\ \textit{Bottom:} \quad & y_n = \left(\frac{L}{V}\right)_B (x_{n+1} - x_B) + x_B \end{aligned} \tag{2.25}$$

A typical McCabe-Thiele diagram is shown in Figure 2.6:

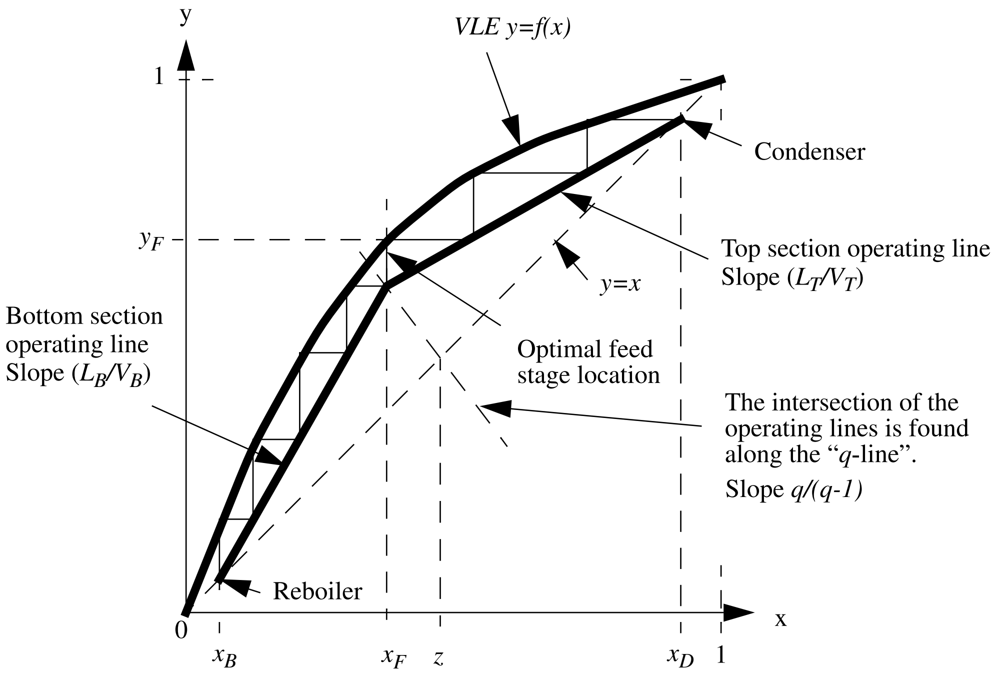

Figure 2.6: McCabe-Thiele Diagram with an optimally located feed.

The optimal feed stage is at the intersection of the two operating lines and the feed stage composition (x_F, y_F) is then equal to the composition of the flashed feed mixture. We have that $z = qx_F + (1-q)y_F$. For $q=1$ (liquid feed) we find $x_F = z$ and for $q=0$ (vapour feed) we find $y_F = z$ (in the other cases we must solve the equation together with the VLE). The pinch, which occurs at one side of the feed stage if the feed is not optimally located, is easily understood from the McCabe-Thiele diagram as shown in Figure 2.8:

2.3.4 Typical Column Profiles — Pinch

An example of a column composition profile is shown in Figure 2.7 for a column with z=0.5, α=1.5, N=40, N_F=21 (counted from the bottom, including the reboiler), y_D=0.90, x_B=0.002. This is a case were the feed stage is not optimally located, as seen from the presence of a pinch zone (a zone of constant composition) above the stage. The corresponding McCabe-Thiele diagram is shown in Figure 2.8: We see that the feed stage is not located at the intersection of the two operating lines, and that there is a pinch zone above the feed, but not below.

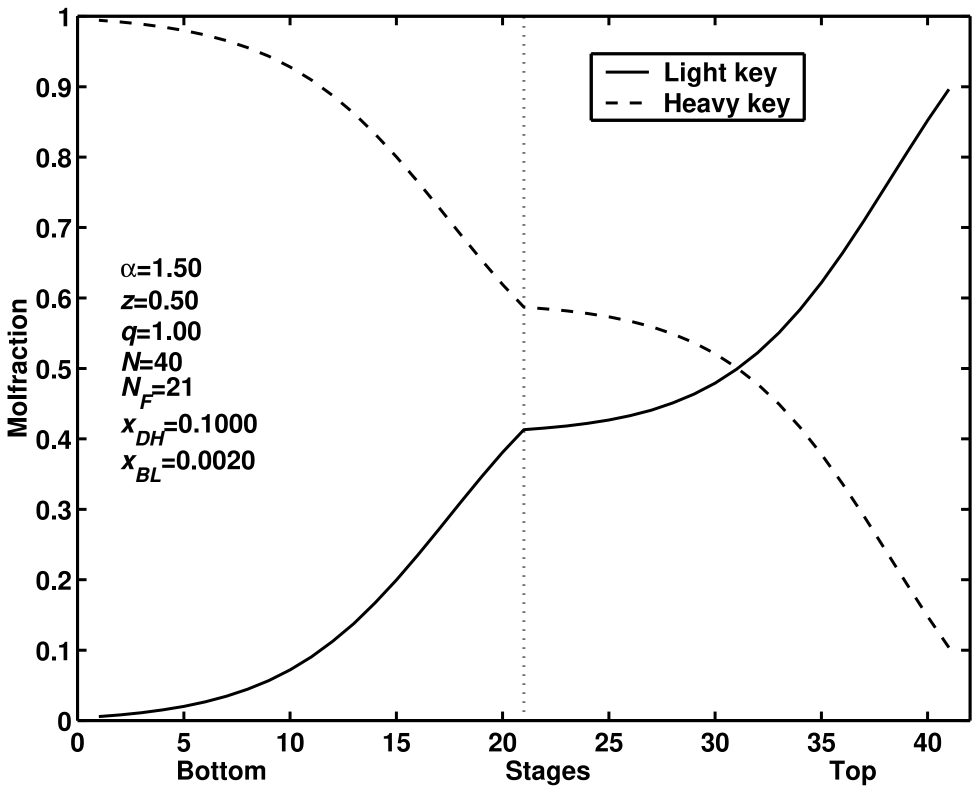

Figure 2.7: Composition profile (x_L,x_H) for case with non-optimal feed location.

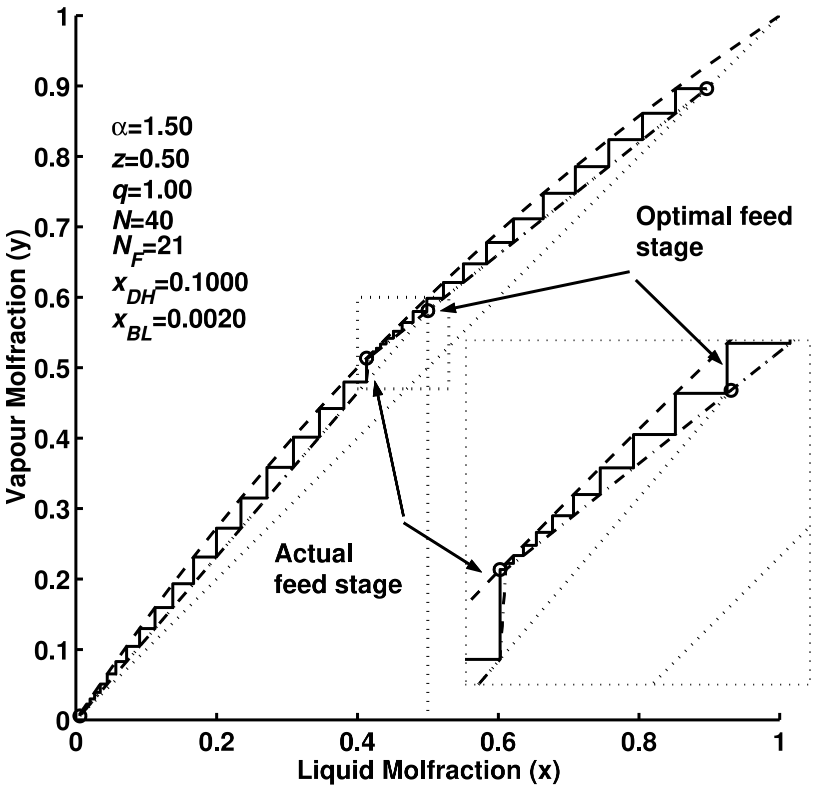

Figure 2.8: McCabe-Thiele diagram for the same example as in Figure 2.7: Observe that the feed stage location is not optimal.

2.4 Simple Design Equations

2.4.1 Minimum Number of Stages — Infinite Energy

The minimum number of stages for a given separation (or equivalently, the maximum separation for a given number of stages) is obtained with infinite internal flows (infinite energy) per unit feed. (This always holds for single-feed columns and ideal mixtures, but may not hold, for example, for extractive distillation with two feed streams.)

With infinite internal flows ("total reflux") $L_n/F=\infty$ and $V_n/F=\infty$, a material balance across any part of the column gives $V_n = L_{n+1}$, and similarly a material balance for any component gives $V_n y_n = L_{n+1} x_{n+1}$. Thus, $y_n = x_{n+1}$, and with constant relative volatility we have:

$$\alpha = \frac{y_{L,n}}{y_{H,n}} \Big/ \frac{x_{L,n}}{x_{H,n}} = \frac{x_{L,n+1}}{x_{H,n+1}} \Big/ \frac{x_{L,n}}{x_{H,n}} \tag{2.26}$$

For a column or column section with N stages, repeated use of this relation gives directly Fenske's formula for the overall separation factor:

$$S = \left(\frac{x_L}{x_H}\right)_T \Big/ \left(\frac{x_L}{x_H}\right)_B = \alpha^N \tag{2.27}$$

For a column with a given separation, this yields Fenske's formula for the minimum number of stages:

$$N_{min} = \frac{\ln S}{\ln \alpha} \tag{2.28}$$

These Fenske expressions do not assume constant molar flows and apply to the separation between any two components with constant relative volatility. Note that although a high-purity separation (large S) requires a larger number of stages, the increase is only proportional to the logarithm of separation factor. For example, increasing the purity level in a product by a factor of 10 (e.g. by reducing $x_{H,D}$ from 0.01 to 0.001) increases N_{min} by about a factor of $\ln 10 = 2.3$.

A common rule of thumb is to select the actual number of stages $N = 2N_{min}$ (or even larger).

2.4.2 Minimum Energy Usage — Infinite Number of Stages

For a given separation, an increase in the number of stages will yield a reduction in the reflux (or equivalently in the boilup). However, as the number of stages approach infinity, a pinch zone develops somewhere in the column, and the reflux cannot be reduced further. For a binary separation the pinch usually occurs at the feed stage (where the material balance line and the equilibrium line will meet), and we can easily derive an expression for the minimum reflux with $N = \infty$. For a saturated *liquid feed* ($q=1$) (King's formula):

$$L_{Tmin} = \frac{r_{L,D} - \alpha r_{H,D}}{\alpha - 1} F \tag{2.29}$$

where $r_{L,D} = x_D D/zF$ is the recovery fraction of light component, and $r_{H,D}$ of heavy component, both in the distillate. The value depends relatively weakly on the product purity, and for sharp separations (where $r_{L,D} = 1$ *and* $r_{H,D} = 0$*)*, we have $L_{min} = F/(\alpha - 1)$. Actually, equation (2.29) applies without stipulating constant molar flows or constant α, but then L_{min} is the liquid flow entering the feed stage from above, and α is the relative volatility at feed conditions. A similar expression, but in terms of V_{Bmin} entering the feed stage from below, applies for a saturated *vapour feed* (*q=0*) (King's formula):

$$V_{Bmin} = \frac{r_{H,B} - \alpha r_{L,B}}{\alpha - 1} F \qquad (2.30)$$

For sharp separations we get $V_{Bmin} = F/(\alpha - 1)$. In summary, for a binary mixture with constant molar flows and constant relative volatility, the minimum boilup for *sharp separations* is:

$$\begin{aligned} &\text{Feed liquid, } q=1: \quad V_{Bmin} = \frac{1}{\alpha - 1} F + D \\ &\text{Feed vapour, } q=0: \; V_{Bmin} = \frac{1}{\alpha - 1} F \end{aligned} \qquad (2.31)$$

Note that minimum boilup is independent of the product purity for sharp separations. From this we establish one of the key properties of distillation: *We can achieve any product purity* (even "infinite separation factor") *with a constant finite energy* (as long as it is higher than *the minimum*) *by increasing the number of stages*.

Obviously, this statement does not apply to azeotropic mixtures, for which $\alpha = 1$ for some composition, (but we can get arbitrary close to the azeotropic composition, and useful results may be obtained in some cases by treating the azeotrope as a pseudo-component and using α for this pseudo-separation).

2.4.3 Finite Number of Stages and Finite Reflux

Fenske's formula $S = \alpha^N$ applies to infinite reflux (infinite energy). To extend this expression to real columns with finite reflux we will assume constant molar flows and consider below three approaches:

1. Assume constant K-values and derive the Kremser formulas (exact close to the column end for a high-purity separation).

2. Assume constant relative volatility and derive the following extended Fenske formula (approximate formula for case with optimal feed stage location):

$$S \approx \alpha^N \frac{(L_T/V_T)^{N_T}}{(L_B/V_B)^{N_B}} \tag{2.32}$$

Here N_T is the number of stages in the top section and N_B in the bottom section.

3. Assume constant relative volatility and derive exact expressions. The most used are the Underwood formulas which are particularly useful for computing the minimum reflux (with infinite stages).

2.4.4 Constant K-values — Kremser Formulas

For high-purity separations most of the stages are located in the "corner" parts of the McCabe-Thiele diagram where we according to Henry's law may approximate the VLE-relationship, even for nonideal mixtures, by straight lines;

Bottom of column: $y_L = H_L x_L$ (light component; $x_L \rightarrow 0$)

Top of column: $y_H = H_H x_H$ (heavy component; $x_H \rightarrow 0$)

where H is Henry's constant. (For the case of constant relative volatility, Henry's constant in the bottom is $H_L = \alpha$ and in the top is $H_H = 1/\alpha$). Thus, with constant molar flows, both the equilibrium and mass-balance relationships are linear, and the resulting difference equations are easily solved analytically. For example, at the bottom of the column we derive for the light component:

$$\begin{aligned} x_{L,n+1} &= (V_B/L_B)H_L x_{L,n} + (B/L_B)x_{L,B} \\ &= s x_{L,n} + (1 - V_B/L_B)x_{L,B} \end{aligned} \tag{2.33}$$

where $s = (V_B/L_B)H_L > 1$ is the stripping factor. Repeated use of this equation gives the Kremser formula for stage N_B from the bottom (the reboiler would here be stage zero):

$$x_{L,N_B} = s^{N_B} x_{L,B}[1 + (1 - V_B/L_B)(1 - s^{-N_B})/(s-1)] \tag{2.34}$$

(assumes we are in the region where s is constant, i.e. $x_L \approx 0$).

At the top of the column we have for the heavy component:

$$\begin{aligned} y_{H,n-1} &= (L_T/V_T)(1/H_H)y_{H,n} + (D/V_T)x_{H,D} \\ &= a y_{H,n} + (1 - L_T/V_T)x_{H,D} \end{aligned} \tag{2.35}$$

where $a = (L_T/V_T)/H_H > 1$ is the absorbtion factor. The corresponding Kremser formula for the heavy component in the vapour phase at stage N_T counted from the top of the column (the accumulator is stage zero) is then:

$$y_{H,N_T} = a^{N_T} x_{H,D}[1 + (1 - L_T/V_T)(1 - a^{-N_T})/(a - 1)] \tag{2.36}$$

(assumes we are in the region where a is constant, i.e. $x_H \approx 0$).

For hand calculations one may use the McCabe-Thiele diagram for the intermediate composition region, and the Kremser formulas at the column ends where the use of the McCabe-Thiele diagram is inaccurate.

> Example. *We consider a column with N=40, N_F=21, α =1.5, z_L=0.5, F=1, D=0.5, V_B=3.2063. The feed is saturated liquid and exact calculations give the product compositions $x_{H,D}$= $x_{L,B}$=0.01.*
> *We now want to have a bottom product with only 1 ppm heavy product, i.e. $x_{L,B}$ = 1.e-6. We can use the Kremser formulas to easily estimate the additional stages needed when we have the same energy usage, V_B=3.2063. (Note that with the increased purity in the bottom we actually get B=0.4949 and L_B=3.7012). At the bottom of the column $H_L = \alpha = 1.5$ and the stripping factor is $s = (V_B/L_B)H_L = (3.2063/3.712)1.5 = 1.2994$. With $x_{L,B}$=1.e-6 (new purity) and $x_{L,N_B} = 0.01$ (old purity) we find by solving the Kremser equation (2.34) with respect to N_B that N_B=33.94, and we conclude that we need about 34 additional stages in the bottom (this is not quite enough since the operating line is slightly moved and thus affects the rest of the column; using 36 rather 34 additional stages compensates for this).*

The above Kremser formulas are valid at the column ends, but the linear approximation resulting from the Henry's law approximation lies above the real VLE curve (is optimistic), and thus gives too few stages in the middle of the column. However, if the there is no pinch at the feed stage (i.e. the feed is optimally located), then most of the stages in the column will be located at the columns ends where the above Kremser formulas apply.

2.4.5 Approximate Formula with Constant Relative Volatility

We will now use the Kremser formulas to derive an approximation for the separation factor S. First note that for cases with high-purity products we have $S \approx 1/(x_{L,B}x_{H,D})$ That is, the separation factor is the inverse of the product of the key component product impurities.

We now assume that the feed stage is optimally located such that the composition at the feed stage is the same as that in the feed, i.e. $y_{H,N_T} = y_{H,F}$ and $x_{L,N_B} = x_{L,F}$ Assuming constant relative volatility and using $H_L = \alpha$, $H_B = 1/\alpha$, $\alpha = (y_{LF}/x_{LF})/(y_{HF}/x_{HF})$ and $N = N_T + N_B + 1$ (including total reboiler) then gives:

$$S \approx \alpha^N \frac{(L_T/V_T)^{N_T}}{(L_B/V_B)^{N_B}} \frac{c}{(x_{HF}y_{LF})} \tag{2.37}$$

$$\text{where } c = \left[1 + \left(1 - \frac{V_B}{L_B}\right)\frac{(1 - s^{-N_B})}{(s-1)}\right]\left[1 + \left(1 - \frac{L_T}{V_T}\right)\frac{(1 - a^{-N_T})}{(a-1)}\right] \tag{2.38}$$

We know that S predicted by this expression is somewhat too large because of the linearized VLE. However, we may correct it such that it satisfies the exact relationship $S = \alpha^N$ at infinite reflux (where $L_B/V_B = V_T/L_T = 1$ and c=1) by dropping the factor $1/(x_{HF}y_{LF})$ (which as expected is always larger than 1). At finite reflux, there are even more stages in the feed region and the formula will further oversestimate the value of S. However, since c > 1 at finite reflux, we may partly counteract this by setting $c=1$. Thus, we delete the term c and arrive at the final extended Fenske formula, where the main assumptions are that we have constant relative volatility, constant molar flows, and that there is no pinch zone around the feed (i.e. the feed is optimally located):

$$S \approx \alpha^N \frac{(L_T/V_T)^{N_T}}{(L_B/V_B)^{N_B}} \tag{2.39}$$

where $N = N_T + N_B + 1$.

Together with the material balance, $Fz_F = Dx_D + Bx_B$, this approximate formula can be used for estimating the number of stages for column design (instead of e.g. the Gilliand plots), and also for estimating the effect of changes of internal flows during column operation. However, its main value is the insight it provides:

1. We see that the best way to increase the separation S is to increase the number of stages.
2. During operation where N is fixed, the formula provides us with the important insight that the separation factor S is increased by increasing the *internal* flows L and V, thereby making L/V closer to 1. However, the effect of increasing the internal flows (energy) is limited since the maximum separation with infinite flows is $S = \alpha^N$.
3. We see that the separation factor S depends mainly on the internal flows (energy usage) and only weakly on the split D/F. This means that if we change D/F then S will remain approximately constant (Shinskey's rule), that is, we will get a shift in impurity from one product to the other such that the product of the impurities remains constant. This insight is very useful.

   Example. *Consider a column with $x_{D,H} = 0.01$ (1% heavy in top) and $x_{B,L} = 0.01$ (1% light in bottom). The separation factor is then approximately $S = 0.99 \times 0.99/(0.01 \times 0.01) = 9801$ Assume we slightly increase D from 0.50 to 0.51. If we assume constant separation factor (Shinskey's rule), then we find that $x_{D,H}$ changes from 0.01 to 0.0236 (heavy impurity in the top product increases by a factor 2.4), whereas and $x_{B,L}$ changes from 0.01 to 0.0042 (light impurity in the bottom product decreases by a factor 2.4). Exact calculations with column data: N=40, N_F=21, α=1.5, z_L=0.5, F=1, D=0.5, L_T/F=3.206, give that $x_{D,H}$ changes from 0.01 to 0.0241 and $x_{B,L}$ changes from 0.01 to 0.0046 (separation factor changes from S=9801 to 8706). Thus, Shinskey's rule gives very accurate predictions.*

However, the simple extended Fenske formula also has shortcomings. First, it is somewhat misleading since it suggests that the separation may always be improved by transferring stages from the bottom to the top section if $(L_T/V_T) > (V_B/L_B)$. This is not generally true (and is not really "allowed" as it violates the assumption of optimal feed location). Second, although the formula gives the correct limiting value $S = \alpha^N$ for infinite reflux, it overestimates the value of S at lower reflux rates. This is not surprising since at low reflux rates a pinch zone develops around the feed.

> Example: *Consider again the column with N=40. N_F=21, α =1.5, z_L=0.5, F=1, D=0.5; L_T=2.706 Exact calculations based on these data give x_{HD}= x_{LB}=0.01 and S = 9801. On the other hand, the extended Fenske formula with N_T=20 and N_B=20 yields:*
>
> $$S = 1.5^{41} \times \frac{(2.7606/3.206)^{20}}{(3.706/3.206)^{20}} = 16586000 \times \frac{0.34}{18.48} = 30774$$
>
> *corresponding to x_{HD}= x_{LB} = 0.0057. The error may seem large, but it is actually quite good for such a simple formula.*

2.4.6 Optimal Feed Location

The optimal feed stage location is at the intersection of the two operating lines in the McCabe-Thiele diagram. The corresponding optimal feed stage composition (x_F, y_F) can be obtained by solving the following two equations: $z = qx_F + (1-q)y_F$ and $y_F = \alpha x_F / (1 + (\alpha - 1)x_F)$. For q=1 (liquid feed) we find $x_F = z$ and for q=0 (vapour feed) we find $y_F = z$ (in the other cases we must solve a second order equation).

There exists several simple shortcut formulas for estimating the feed point location. One may derived from the Kremser equations given above. Divide the Kremser equation for the top by the one for the bottom and assume that the feed is optimally located to derive:

$$\frac{y_{H,F}}{x_{L,F}} = \frac{x_{H,D}}{x_{L,B}} \alpha^{(N_T - N_B)} \frac{\left(\frac{L_T}{V_T}\right)^{N_T} \left[1 + \left(1 - \frac{L_T}{V_T}\right)\frac{(1 - a^{-N_T})}{(a-1)}\right]}{\left(\frac{V_B}{L_B}\right)^{N_B} \left[1 + \left(1 - \frac{V_B}{L_B}\right)\frac{(1 - s^{-N_B})}{(s-1)}\right]} \tag{2.40}$$

The last "big" term is close to 1 in most cases and can be neglected. Rewriting the expression in terms of the light component then gives Skogestad's shortcut formula for the feed stage location:

$$N_T - N_B = \frac{\ln\left(\left[\frac{(1-y_F)}{x_F}\right]\left[\frac{x_B}{(1-x_D)}\right]\right)}{\ln\alpha} \tag{2.41}$$

where y_F and x_F at the feed stage are obtained as explained above. The optimal feed stage location counted from the bottom is then:

$$N_F = N_B + 1 = \frac{[N + 1 - (N_T - N_B)]}{2} \tag{2.42}$$

where N is the total number of stages in the column.

2.4.7 Summary for Continuous Binary Columns

With the help of a few of the above formulas it is possible to perform a column design in a matter of minutes by hand calculations. We will illustrate this with a simple example.

We want to design a column for separating a saturated vapour mixture of 80% nitrogen (L) and 20% oxygen (H) into a distillate product with 99% nitrogen and a bottoms product with 99.998% oxygen (mole fractions).

Component data: Normal boiling points (at 1 atm): T_{bL} = 77.4K, T_{bH} = 90.2K, heat of vaporization at normal boiling points: 5.57 kJ/mol (L) and 6.82 kJ/mol (H).

The calculation procedure when applying the simple methods presented in this article can be done as shown in the following steps:

1. Relative volatility:

   The mixture is relatively ideal and we will assume constant relative volatility. The estimated relative volatility at 1 atm based on the boiling points is $\ln\alpha \approx \frac{\Delta\bar{H}^{vap}}{R\bar{T}_b}\frac{(T_{bH} - T_{bL})}{\bar{T}_b}$ where

   $\Delta\bar{H}^{vap} = \sqrt{5.57 \cdot 6.82} = 6.16\ kJ/mol$, $\bar{T}_b = \sqrt{T_{bH}T_{bL}} = 83.6K$ and $T_H - T_L = 90.2 - 77.7 = 18.8$. This gives $(\Delta\bar{H}^{vap})/(R\bar{T}_b) = 8.87$ and we find $\alpha \approx 3.89$ (however, it is generally recommended to obtain α from experimental VLE data).

2. Product split:

   From the overall material balance we get

   $$\frac{D}{F} = \frac{z - x_B}{x_D - x_B} = \frac{0.8 - 0.00002}{0.99 - 0.00002} = 0.808\,.$$

3. Number of stages:

   The separation factor is $S = \frac{0.99 \times 0.99998}{0.01 \times 0.00002} = 4950000$, i.e. ln S = 15.4.

   The minimum number of stages required for the separation is $N_{min} = \ln S / \ln\alpha = 11.35$ and we select the actual number of stages as $N = 23$ ($\approx 2N_{min}$).

4. Feed stage location

   With an optimal feed location we have at the feed stage ($q=0$) that $y_F = z_F$ = 0.8 and $x_F = y_F / (\alpha - (\alpha - 1) y_F) = 0.507$.

   Skogestad's approximate formula for the feed stage location gives

   $$N_T - N_B = \ln\left(\left[\frac{(1-y_F)}{x_F}\right]\left[\frac{x_B}{(1-x_D)}\right]\right) / (\ln\alpha)$$

   $$= \ln\left(\left[\frac{0.2}{0.507}\right] \times \left[\frac{0.00002}{0.01}\right]\right) / 1.358 = -5.27$$

   corresponding to the feed stage $N_F = [N + 1 - (N_T - N_B)]/2 = (23 + 1 + 5.27)/2 = 14.6 \approx 15$.

5. Energy usage:

   The minimum energy usage for a vapour feed (assuming sharp separation) is $V_{min}/F = 1/(\alpha - 1) = 1/2.89 = 0.346$. With the choice $N = 2N_{min}$, the actual energy usage (V) is then typically about 10% above the minimum (V_{min}), i.e. V/F is about 0.38.

This concludes the simple hand calculations. Note again that the number of stages depends directly on the product purity (although only logarithmically), whereas for well-designed columns (with a sufficient number of stages) the energy usage is only weakly dependent on the product purity.

Remark 1:

The actual minimum energy usage is slightly lower since we do not have sharp separations. The recovery of the two components in the bottom product is $r_L = (x_{L,B}B)/(z_{FL}F) = 0.9596$ and

$r_H = (x_{H,B}B)/(z_{FH}F) \approx 0$, so from the formulas given earlier the exact value for nonsharp separations is

$V_{min}/F = (0.9596 - 0.0 \times 3.89)/(3.89 - 1) = 0.332$

Remark 2:

For a liquid feed we would have to use more energy, and for a sharp separation

$$V_{min}/F = 1/(\alpha - 1) + D/F = 0.346 + 0.808 = 1.154$$

Remark 3:

We can check the results with exact stage-by-stage calculations. With N=23, N_F=15 and α=3.89 (constant), we find V/F = 0.374 which is about 13% higher than V_{min}=0.332.

Remark 4:

A simulation with more rigorous VLE computations, using the SRK equation of state, has been carried out using the HYSYS simulation package. The result is a slightly lower vapour flow due to a higher relative volatility (α in the range from 3.99-4.26 with an average of 4.14). More precisely, a simulation with N=23, N_F=15 gave V/F=0.291, which is about 11% higher than the minimum value $V'_{min} = 0.263$ found with a very large number of stages (increasing N>60 did not give any significant energy reduction below V'_{min}). The optimal feed stage (with N=23) was found to be N_F=15.

Thus, the results from HYSYS confirms that a column design based on the very simple shortcut methods is very close to results from much more rigorous computations.

2.5 Multicomponent Distillation — Underwood's Methods

We here present the Underwood equations for multicomponent distillation with constant relative volatility and constant molar flows. The analysis is based on considering a two-product column with a single feed, but the usage can be extended to all kind of column section interconnections.

It is important to note that adding more components does not give any additional degrees of freedom in operation. This implies that for an ordinary two-product distillation column we still have only two degrees of freedom, and thus, we will only be able to specify two variables, e.g. one property for each product. Typically, we specify the purity (or recovery) of the light key in the top, and specify the heavy key purity in the bottom (the key components are defined as the components between which we are performing the split). The recoveries for all other components and the internal flows (*L* and *V*) will then be completely determined.

For a binary mixture with given products, as we increase the number of stages, there develops a pinch zone on both sides of the feed stage. For a multicomponent mixture, a feed region pinch zone only develops when all components distribute to both products, and the minimum energy operation is found for a particular set of product recoveries, sometimes denoted as the "preferred split". If all components do not distribute, the pinch zones will develop away from the feed stage. Underwood's methods can be used in all these cases, and are especially useful for the case of infinite number of stages.

2.5.1 The Basic Underwood Equations

The net material transport (w_i) of component *i* upwards through a stage *n* is:

$$w_i = V_n y_{i,n} - L_{n+1} x_{i,n+1} \tag{2.43}$$

Note that w_i is constant in each column section. We assume constant molar flows ($L=L_n=L_{n-1}$ *and* $V=V_n=V_{n+1}$), and assume constant relative volatility. The VLE relationship is then:

$$y_i = \frac{\alpha_i x_i}{\sum_i \alpha_i x_i} \quad \text{where } \alpha_i = \frac{(y_i/x_i)}{(y_r/x_r)} \tag{2.44}$$

We divide equation (2.43) by *V*, multiply it by the factor $\alpha_i/(\alpha_i - \phi)$, and take the sum over all components:

$$\frac{1}{V}\sum_i \frac{\alpha_i w_i}{(\alpha_i - \phi)} = \frac{\sum_i \frac{\alpha_i^2 x_{i,n}}{(\alpha_i - \phi)}}{\sum_i \alpha_i x_{i,n}} - \frac{L}{V}\sum_i \frac{\alpha_i x_{i,n+1}}{(\alpha_i - \phi)} \tag{2.45}$$

The parameter ϕ is free to choose, and the Underwood roots are defined as the values of ϕ which make the left hand side of (2.45) unity, i.e which satisfy

$$V = \sum_{i=1}^{Nc} \frac{\alpha_i w_i}{(\alpha_i - \phi)} \tag{2.46}$$

The number of values ϕ satisfying this equation is equal to the number of components, N_c.

Comment: Most authors use a product composition (x) or component recovery (r) in this definition, e.g for the top (subscript T) section or the distillate product (subscript D):

$$w_i = w_{i,T} = w_{i,D} = Dx_{i,D} = r_{i,D} z_i F \tag{2.47}$$

but we prefer to use the net component molar flow (w) since it is more general. Note that use of the recovery is equivalent to using net component flow, but use of the product composition is only applicable when a single product stream is leaving the column. If we apply the product recovery, or the product composition, the defining equation for the top section becomes:

$$V_T = \sum_i \frac{\alpha_i r_{i,D} z_i}{(\alpha_i - \phi)} F = \sum_i \frac{\alpha_i x_{i,D}}{(\alpha_i - \phi)} D \tag{2.48}$$

2.5.2 Stage to Stage Calculations

By the definition of ϕ from (2.46), the left hand side of (2.45) equals one, and the last term of (2.45) then equals:

$$\frac{\sum_i \frac{\alpha_i^2 x_{i,n}}{(\alpha_i - \phi)}}{\sum_i \alpha_i x_{i,n}} - 1 = \frac{\sum_i \left(\frac{\alpha_i^2 x_{i,n}}{(\alpha_i - \phi)} - \alpha_i x_{i,n} \right)}{\sum_i \alpha_i x_{i,n}} = \frac{\sum_i \frac{(\alpha_i^2 x_{i,n} - (\alpha_i - \phi)\alpha_i x_{i,n})}{(\alpha_i - \phi)}}{\sum_i \alpha_i x_{i,n}}$$

The terms with α_i^2 disappear in the nominator and ϕ can be taken outside the summation, thus (2.45) is simplified to:

$$\frac{L}{V}\sum_i \frac{\alpha_i x_{i,n+1}}{(\alpha_i - \phi)} = \frac{\phi \sum_i \frac{\alpha_i x_{i,n}}{(\alpha_i - \phi)}}{\sum_i \alpha_i x_{i,n}} \tag{2.49}$$

This equation is valid for any of the Underwood roots, and if we assume constant molar flows and divide an equation for ϕ_k with the one for ϕ_j, the following expression appears:

$$\left(\frac{\sum_i \frac{\alpha_i x_{i,n+m}}{(\alpha_i - \phi_k)}}{\sum_i \frac{\alpha_i x_{i,n+m}}{(\alpha_i - \phi_j)}}\right) = \left(\frac{\phi_k}{\phi_j}\right)^m \left(\frac{\sum_i \frac{\alpha_i x_{i,n}}{(\alpha_i - \phi_k)}}{\sum_i \frac{\alpha_i x_{i,n}}{(\alpha_i - \phi_j)}}\right) \tag{2.50}$$

and we note the similarities with the Fenske and Kremser equations derived earlier. This relates the composition on a stage (n) to an composition on another stage (n+m). The number of independent equations of this kind equals the number of Underwood roots minus 1 (since the number of equations of the type as in equation (2.49) equals the number of Underwood roots), but in addition we also have $\sum x_i = 1$. Together, this is a linear equation system for computing $x_{i,n+m}$ when $x_{i,n}$ is known and the Underwood roots is computed from (2.46).

Note that so far we have not discussed minimum reflux (or vapour flow rate), thus these equation holds for any vapour and reflux flow rates, provided that the roots are computed from the definition in (2.46).

2.5.3 Some Properties of the Underwood Roots

Underwood showed a series of important properties of these roots for a two-product column with a reboiler and condenser. In this case all components flow upwards in the top section ($w_{i,T} \geq 0$), and downwards in the bottom section ($w_{i,B} \leq 0$). The mass balance yields: $w_{i,B} = w_{i,T} - w_{i,F}$ where $w_{i,F} = Fz_i$. Underwood showed that in the top section (with N_c components) the roots (ϕ) obey:

$$\alpha_1 > \phi_1 > \alpha_2 > \phi_2 > \alpha_3 > \ldots > \alpha_{Nc} > \phi_{Nc} \tag{2.51}$$

And in the bottom section (where $w_{i,n} = w_{i,B} \le 0$) we have a different set of roots denoted (ψ) computed from

$$V_B = \sum_i \frac{\alpha_i w_{i,B}}{(\alpha_i - \psi)} = \sum_i \frac{\alpha_i(-r_{i,B})z_i F}{(\alpha_i - \psi)} = \sum_i \frac{\alpha_i(-(1-r_{i,D}))z_i F}{(\alpha_i - \psi)} \qquad (2.52)$$

$$\text{which obey:}\ \psi_1 > \alpha_1 > \psi_2 > \alpha_2 > \psi_3 > \alpha_3 > \ldots > \psi_{Nc} > \alpha_{Nc} \qquad (2.53)$$

Note that the smallest root in the top section is smaller than the smallest relative volatility, and the largest root in the bottom section is larger then the largest volatility. It is easy to see from the defining equations that as $V_T \to \infty \quad \Rightarrow \quad \phi_i \to \alpha_i$ and similarly as $V_B \to \infty \quad \Rightarrow \quad \psi_i \to \alpha_i$.

When the vapour flow is reduced, the roots in the top section will decrease, while the roots in the bottom section will increase, but interestingly Underwood showed that $\phi_i \ge \psi_{i+1}$. A very important result by Underwood is that for infinite number of stages; $V \to V_{min} \quad \Rightarrow \quad \phi_i \to \psi_{i+1}$.

Thus, at minimum reflux, the Underwood roots for the top (ϕ) and bottom (ψ) sections coincide. Thus, if we denote these common roots θ, and recall that $V_T - V_B = (1-q)F$, and that $w_{i,T} - w_{i,B} = w_{i,F} = z_i F$ we obtain the following equation for the "minimum reflux" common roots (θ) by subtracting the defining equations for the top and bottom sections:

$$(1-q) = \sum_i \frac{\alpha_i z_i}{(\alpha_i - \theta)} \qquad (2.54)$$

We denote this expression the feed equation since only the feed properties (q and z) appear. Note that this is not the equation which defines the Underwood roots and the solutions (θ) apply as roots of the defining equations only for minimum reflux conditions ($N = \infty$). The feed equation has N_c roots, (but one of these is not a common root) and the N_c-1 common roots obey: $\alpha_1 > \theta_1 > \alpha_2 > \theta_2 > \ldots > \theta_{Nc-1} > \alpha_{Nc}$. Solution of the feed equation gives us the possible common roots, but all pairs of roots (ϕ_i *and* ψ_{i+1}) for the top and bottom section do not necessarily coincide for an arbitrary operating condition. We illustrate this with the following example:

Assume we start with a given product split (*D/F*) and a large vapour flow (*V/F*). Then only one component *i* (with relative volatility α_i) can be distributed to both products. No roots are common. Then we gradually reduce *V/F* until a second component *j* (this has to be a component $j=i+1$ or $j=i-1$) becomes distributed. E.g for $j=i+1$ one set of roots will coincide: $\phi_i = \psi_{i+1} = \theta_i$, while the others do not. As we reduce *V/F* further, more components become distributed and the corresponding roots will coincide, until all components are distributed to both products, and then all the N_c-*1* roots from the feed equation also are roots for the top and bottom sections.

An important property of the Underwood roots is that the value of a pair of roots which coincide (e.g. when $\phi_i = \psi_{i+1} = \theta_i$) will not change, even if only one, two or all pairs coincide. Thus all the possible common roots are found by solving the feed equation once.

2.5.4 Minimum Energy — Infinite Number of Stages

When we go to the limiting case of infinite number of stages, Underwoods's equations become very useful. The equations can be used to compute the minimum energy requirement for any feasible multicomponent separation.

Let us consider two cases: First we want to compute the minimum energy for a sharp split between two adjacent key components *j* and *j+1* ($r_{j,D} = 1$ and $r_{j+1,D} = 0$). The procedure is then simply:

1. Compute the common root (θ_j) for which $\alpha_j > \theta_j > \alpha_{j+1}$

   from the feed equation: $(1-q) = \sum_i \frac{a_i z_i}{(a_i - \theta)}$

2. Compute the minimum energy by applying the definition equation for θ_j.

   $$\frac{V_{Tmin}}{F} = \sum_{i=1}^{j} \frac{a_i z_i}{(a_i - \theta_j)}.$$

   Note that the recoveries $r_{i,D} = \begin{cases} 1 & for\ i \le j \\ 0 & for\ i > j \end{cases}$

For example, we can derive Kings expressions for minimum reflux for a binary feed ($z_L = z$, $z_H = (1-z)$, $\alpha_L = \alpha, \alpha_H = 1$, and liquid feed ($q=1$)). Consider the case with liquid feed (q=1). We find the single common root from the feed equation: $\theta = \alpha/(1+(\alpha-1)z)$, (observe $\alpha \ge \theta \ge 1$ as expected). The minimum reflux expression appears as we use the defining equation with the common root:

$$\frac{L_{Tmin}}{F} = \frac{V_{Tmin}}{F} - \frac{D}{F} = \sum_i \frac{\theta r_{i,D} z_i}{(\alpha_i - \theta)} = \frac{\theta r_{L,D} z}{\alpha - \theta} + \frac{\theta r_{H,D}(1-z)}{1-\theta} \tag{2.55}$$

and when we substitute for θ and simplify, we obtain King's expression:

$$\frac{L_{Tmin}}{F} = \frac{r_{L,D} - \alpha r_{H,D}}{\alpha - 1} \tag{2.56}$$

Another interesting case is minimum energy operation when we consider sharp split only between the most heavy and most light components, while all the intermediates are distributed to both products. This case is also denoted the "preferred split", and in this case there will be a pinch region on both sides of the feed stage. The procedure is:

1. Compute all the N_c-1 common roots (θ)from the feed equation.
2. Set $r_{1,D} = 1$ and $r_{N_c,D} = 0$ and solve the following linear equation set ($N_c - 1$ equations) with respect to $[V_T, r_{2,D}, r_{3,D} \ldots r_{N_c-1}]$ ($N_c - 1$ variables):

$$\begin{gathered} V_T = \sum_{i=1}^{N_c} \frac{a_i r_{i,D} z_i}{(a_i - \theta_1)} \\ \bullet \\ \bullet \\ V_T = \sum_{i=1}^{N_c} \frac{a_i r_{i,D} z_i}{(a_i - \theta_{N_c-1})} \end{gathered} \tag{2.57}$$

Note that in this case, when we regard the most heavy and light components as the keys, and all the intermediates are distributed to both products and Kings very simple expression will also give the correct minimum reflux for a multicomponent mixture (for $q=1$ or $q=0$). The reason is that the pinch then occurs at the feed stage. In general, the values computed by Kings expression give a (conservative) *upper bound* when applied directly to multicomponent mixtures. An interesting result which can be seen from Kings's formula is that the minimum reflux at preferred split (for q=1) is independent of the feed composition and also independent of the relative volatilities of the intermediates.

However, with the more general Underwood method, we also obtain the distribution of the intermediates, and it is easy to handle any liquid fraction (q) in the feed.

The procedure for an arbitrary feasible product recovery specification is similar to the preferred split case, but then we must only apply the Underwood roots (and corresponding equations) with values between the relative volatilities of the distributing components and the components at the limit of being distributed. In cases where not all components distribute, King's minimum reflux expression cannot be trusted directly, but it gives a (conservative) *upper bound*.

Figure 2.9 shows an example of how the components are distributed to the products for a ternary (ABC) mixture. We choose the overhead vapour flow ($V=V_T$) and the distillate product flow ($D=V$-L) as the two degrees of freedom. The straight lines, which are at the boundaries when a component is at the limit of appearing/disappearing (distribute/not distribute) in one of the products, can be computed directly by Underwood's method. Note that the two peaks (P_{AB} and P_{BC}) gives us the minimum vapour flow for sharp split between A/B and B/C. The point P_{AC}, however, is at the minimum vapour flow for sharp
A/C split and this occurs for a specific distribution of the intermediate B, known as the "preferred split".

Kings's minimum reflux expression is only valid in the triangle below the preferred split, while the Underwood equations can reveal all component recoveries for all possible operating points. (The shaded area is not feasible since all liquid and vapour streams above and below the feed have to be positive).

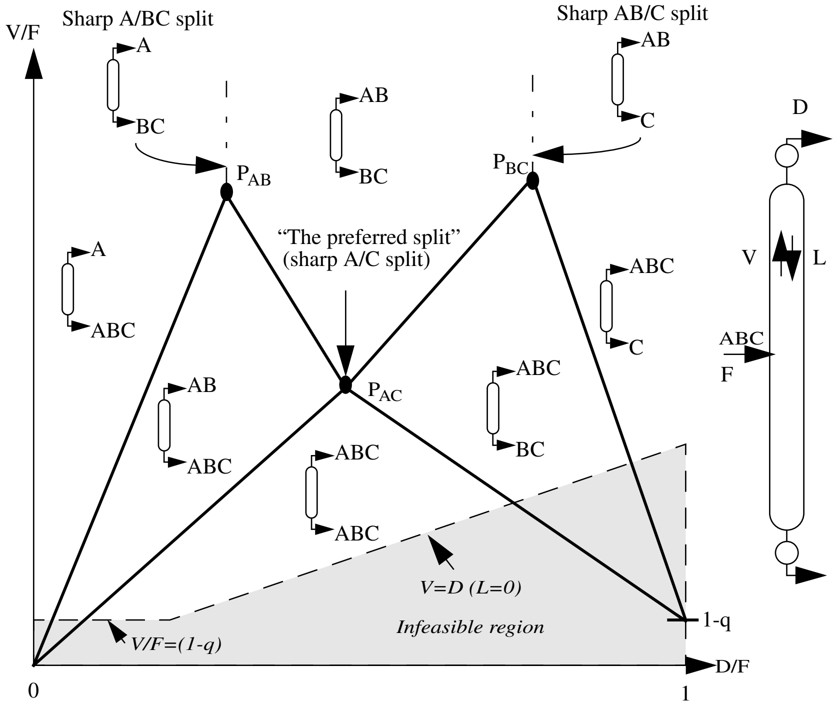

Figure 2.9: Regions of distributing feed components as function of *V* and *D* for a feed mixture with three components: ABC. P_{ij} represent minimum energy for sharp split between component *i* and *j*. For large vapour flow (above the top "saw-tooth"), only one component distribute. In the triangle below P_{AC}, all components distribute.

2.6 Further Discussion of Specific Issues

2.6.1 The Energy Balance and the Assumption of Constant Molar flows

All the calculations in this article are based on the assumption of constant molar flows in a section, i.e $V_n = V_{n-1} = V$ and $L_n = L_{n+1} = L$. This is a very common simplification in distillation computations, and we shall use the energy balance to see when we can justify it. The energy balance is similar to the mass balance, but now we use the molar enthalpy (h) of the streams instead of composition. The enthalpy is computed for the actual mixture and will be a function of composition in addition to temperature (or pressure). At steady state the energy balance around stage n becomes:

$$L_n h_{L,n} - V_{n-1} h_{V,n-1} = L_{n+1} h_{L,n+1} - V_n h_{V,n} \qquad (2.58)$$

Combining this energy balance with the overall material balance on a stage ($V_{n-1} - L_n = V_n - L_{n+1} = W$ where W is the net total molar flow through a section, i.e. W=D in the top section and -W=B in the bottom section) yields:

$$V_n = V_{n-1}\frac{h_{V,n-1} - h_{L,n}}{h_{V,n} - h_{L,n+1}} + W\frac{h_{L,n} - h_{L,n+1}}{h_{V,n} - h_{L,n+1}} \qquad (2.59)$$

From this expression we observe how the vapour flow will vary through a section due to variations in heat of vaporization and molar enthalpy from stage to stage.

We will now show one way of deriving the constant molar flow assumption:

1. Chose the reference state (where h=0) for each pure component as saturated liquid at a reference pressure. (This means that each component has a different reference temperature, namely its boiling point (T_{bpi}) at the reference pressure.)
2. Assume that the column pressure is constant and equal to the reference pressure.
3. Neglect any heat of mixing such that $h_{L,n} = \sum_i x_{i,n} c_{PLi}(T_n - T_{bpi})$.
4. Assume that all components have the same molar heat capacity c_{PL}.
5. Assume that the stage temperature can be approximated by $T_n = \sum_i x_{i,n} T_{bpi}$. These assumptions gives $h_{L,n} = 0$ on all stages and the equation (2.59) for change in boilup is reduced to:

$$V_n = V_{n-1}\frac{h_{V,n-1}}{h_{V,n}} \qquad (2.60)$$

6. The molar enthalpy in the vapour phase is given as: $h_{V,n} = \sum_i x_{i,n} \Delta H^{vap}_{bpi} + \sum_i x_{i,n} c_{PVi}(T_n - T_{bpi})$ where ΔH^{vap}_{bpi} is the heat of vaporization for the pure component at its reference boiling temperature (T_{bpi}).

7. We assume that c_{PV} is equal for all components, and then the second summation term above will become zero, and we have:
   $h_{V,n} = \sum_i x_{i,n} \Delta H_{bpi}^{vap}$.
8. Then if $\Delta H_{bpi}^{vap} = \Delta H^{vap}$ is equal for all components we get
   $h_{V,n} = h_{V,n-1} = \Delta H^{vap}$, and thereby constant molar flows:
   $V_n = V_{n-1}$ and also $L_n = L_{n+1}$.

At first glance, these assumptions may seem restrictive, but the assumption of constant molar flows actually holds well for many industrial mixtures.

In a binary column where the last assumption about equal ΔH_{bpi}^{vap} is not fulfilled, a good estimate of the change in molar flows from the bottom (stage *1*) to the top (stage *N*) for a case with saturated liquid feed ($q=1$) and close to pure products, is given by: $V_N / V_1 \approx \Delta H_H^{vap} / \Delta H_L^{vap}$. The molar heats of vaporization is taken at the boiling point temperatures for the heavy (H) and light (L) components respectively.

Recall that the temperature dependency of the relative volatility were related to different heat of vaporization also, thus the assumptions of constant molar flows and constant relative volatility are closely related.

2.6.2 Calculation of Temperature when Using Relative Volatilities

It may look like that we have lost the pressure and temperature in the equilibrium equation when we introduced the relative volatility. However, this is not the case since the vapour pressure for every pure component is a direct function of temperature, thus so is also the relative volatility. From the relationship $P = \sum p_i = \sum x_i p_i^o(T)$ we derive:

$$P = p_r^o(T) \sum_i x_i \alpha_i \tag{2.61}$$

Remember that only one of P or T can be specified when the mole fractions are specified. If composition and pressure is known, a rigorous solution of the temperature is found by solving the non-linear equation:

$$P = \sum x_i p_i^o(T) \tag{2.62}$$

However, if we use the pure components boiling points (T_{bi}), a crude and simple estimate can be computed as:

$$T \approx \sum x_i T_{bi} \tag{2.63}$$

For ideal mixtures, this usually give an estimate which is a bit higher than the real temperature, however, similar approximation may be done by using the vapour compositions (y), which will usually give a lower temperature estimate. This leads to a good estimate when we use the average of x and y, i.e:

$$T \approx \sum \left(\frac{x_i + y_i}{2}\right) T_{bi} \tag{2.64}$$

Alternatively, if we are using relative volatilities we may find the temperature via the vapour pressure of the reference component. If we use the Antoine equation, then we have an explicit equation:

$$T \approx \frac{B_r}{\log p_r^o - A_r} + C_r \text{ where } p_r^o = P / \sum_i x_i \alpha_i \tag{2.65}$$

This last expression is a very good approximation to a solution of the nonlinear equation (2.62). An illustration of how the different approximations behave is shown in Figure 2.10: For that particular case (a fairly ideal mixture), equation (2.64) and (2.65) almost coincide..

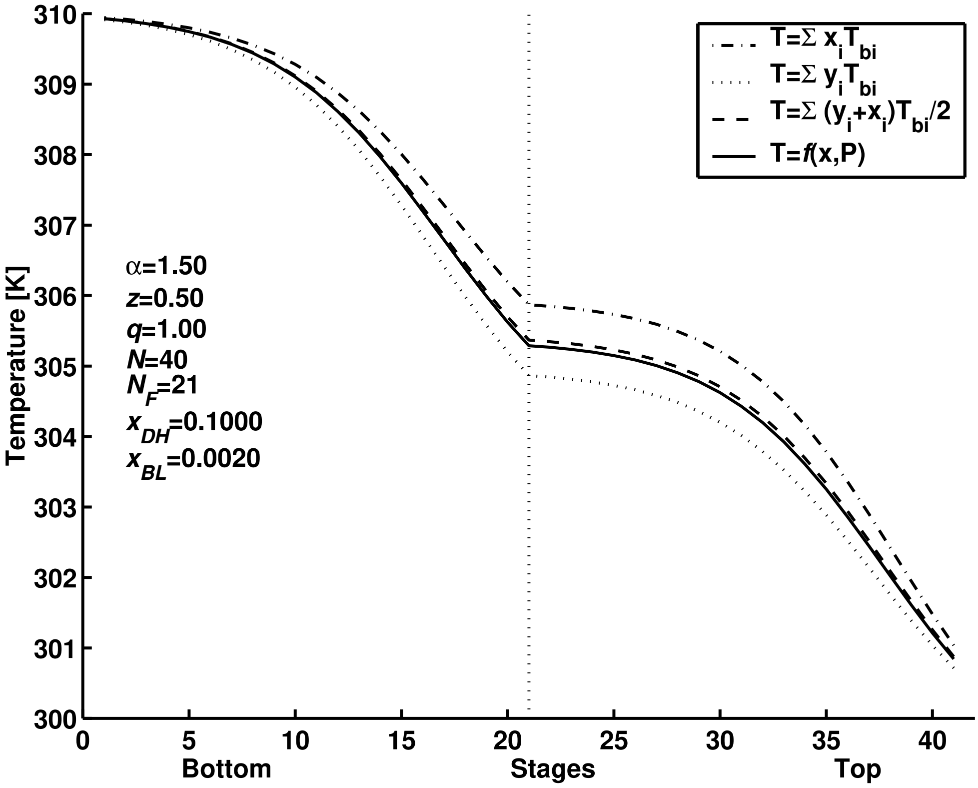

Figure 2.10: Temperature profile for the example in Figure 2.7 (solid line) compared with various linear boiling point approximations.

In a rigorous simulation of a distillation column, the mass and energy balances and the vapour liquid equilibrium (VLE) have to be solved simultaneously for all stages. The temperature is then often used as an iteration parameter in order to compute the vapour-pressures in VLE-computations and in the enthalpy computations of the energy balance.

2.6.3 Discussion and Caution

Most of the methods presented in this article are based on ideal mixtures and simplifying assumptions about constant molar flows and constant relative volatility. Thus there are may separation cases for non-ideal systems where these methods cannot be applied directly.

However, if we are aware about the most important shortcomings, we may still use these simple methods for shortcut calculations, for example, to gain insight or check more detailed calculations.

2.7 Bibliography

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