

# Introductory Unit Operations and Separation Processes

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CHEG 302 Final Project



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# Preface

The goal of this document is to provide a comprehensive guide to the course material of CHEG 302, as well as serve as a useful reference for reviewing the most important material. This goal is both complex and contradictory, as these two use cases are often at odds with one another. For example, consider the conceptual difference between the questions:

*How does flash distillation work?*  
*What is the operating line for a stripping column?*

A resource for someone looking to reference an important question or be reminded of notational nuances will be very different than a resource intended to teach a student key concepts. It will be left as an exercise to the reader if I have achieved my goal.

One observation I have made in planning and preparing this document is just how little we learned. I have spent weeks and weeks grappling with increasingly more difficult and complicated topics, and yet, upon reflection, it's as if we have barely covered anything. This is a paradox resolved by depth. Consider a miner digging straight down, swinging their pick axe day and night for three months, digging deeper and deeper against increasingly hard stone. Would it be fair to criticize them for having dug a narrow hole?

Despite the lack of breadth, this is after all a 300-level course, we have traversed immense depth with enormous effort. My hope is that this document can also capture the pride I feel, nearing the end of this journey, tirelessly labouring until the end, *infatigable et obstiné*.

Oftentimes, in CHEG 302, I have referenced the sonnets of Joachim Du Bellay, in particular his sonnet N°39, where he wishes he were anywhere but where he was, and laments his responsibilities. He writes that he was born for the Muse, a pseudo-religious calling to the arts, but he must labour in busywork. Typically *le ménage* is better understood as housework, or other menial labour, however, in Engineering I feel have come to understand a new meaning of these words. It is the feeling of ambition and creativity in the face of formulas and algorithms; it is the desperate plea, beneath an impossible amount of work, to be anywhere else, doing anything else.

In this, is the inspiration for this document. I want this document to be professional, sleek, functional... beautiful. I want this for myself, I want this for my Muse. All the hours of frustration, in making this text and throughout this semester should be worthwhile. I would like, at the very least, the satisfaction of purpose. Thus, I have made this for my Muse, and they love me just the same.

This document will not have been easy to create, and has been constructed in the L<sup>A</sup>T<sub>E</sub>X language with the help of countless guides and online resources.

*Je suis né pour la Muse, on me fait ménager*

*Joachim Du Bellay*

# Equilibrium and Two-Phase Systems

A *Separation Process* is a unit operation which increases the concentration of a single component. All processes, both simple and complex, share the same driving force, equilibrium, as the system will always trend from its current state towards the equilibrium state. Separation is, put simply, clever exploitation of this natural trend towards equilibrium.

## What is Equilibrium?

Up until the 1980's, it was common for bars, restaurants, and even airplanes to have smoking sections. The problem with this should be immediately apparent. Release toxic smoke in one corner of a small enclosure, and soon enough the entire room will be saturated with smoke. Why does this occur? What drives the smoke to diffuse evenly across the entire volume? Why don't swimming pools have a pissing section? The answer is *equilibrium*.

**Definition.** *The equilibrium state of the system is the state in which there is net change in concentration over time.*

Systems are constantly in motion, diffusing from one state to another continuously and randomly. The emergent behavior of this randomness is that the system will tend towards the equilibrium state. Once at this state, the system state will remain constant unless an external factor changes the equilibrium state. As a rule, a system at equilibrium will have uniform temperature and pressure.

As an example, imagine a tank comprised of two components in vapor-liquid equilibrium. We will call these components  $A$  and  $B$  and we will refer to the liquid phases and vapour phases as  $x$  and  $y$  respectively. Let  $x_A$  be the fraction of  $A$  in the liquid phase, let  $y_B$  be the fraction of  $B$  in the vapour phase, and so forth. Since

$$x_A + x_B = 1$$

$$y_A + y_B = 1$$

it is conventional to only consider the fraction of component  $A$  since the fraction of component  $B$  can be easily derived thereafter. Note that:

$$x_A + y_A \neq 1$$

as the vapour and liquid fractions are not directly dependant on each other - that's what equilibrium is for! In this system,  $x_A$  and  $y_A$  are in equilibrium, in other words, that  $y_A$  can be expressed as a function of  $x_A$ .

## Vapour-Liquid Equilibrium

The most studied case of equilibrium throughout this course is vapour-liquid equilibrium. This is the equilibrium at play in the previous example: the equilibrium between the fraction of  $A$  in the liquid phase  $x_A$  and the fraction of  $A$  in the vapour phase  $y_A$ . What drives a component to be in the vapour or liquid phase?

**Definition.** *Volatility is the property of a component which describes its capacity to turn into a vapour. Components with lower boiling points can be considered more volatile.*

By convention, in systems exploiting volatility, we call the more volatile component  $A$ . Different components have different volatilities, and it is useful to compare the volatilities of different components.

$$\alpha_{AB} = \frac{P_A/x_A}{P_B/x_B} \geq 1 \quad (1.1)$$

We define  $\alpha_{AB}$  to be the relative volatility of  $A$  and  $B$ , where  $P_A$  is the *partial pressure* of  $A$  and  $x_A$  is the *mole fraction of  $A$  in the liquid phase*.

For certain systems, we can assume that the inter-molecular forces within the liquid and vapor can be ignored. We call this *ideal vapour-liquid equilibrium*. Assuming an ideal system greatly simplifies what is necessary to model a separation, in particular, much can be derived from 1.1.

$$P_A = y_A P \quad (1.2)$$

This is the equation for the partial pressure of  $A$ , where  $P$  represents the total pressure of the system. Substituting equations 1.1 and 1.2 and simplifying, we get

$$\alpha_{AB} = \frac{y_A/x_A}{y_B/x_B} \quad (1.3)$$

This can be rearranged as an equilibrium expression equation:

$$y_A = \frac{x_A \alpha_{AB}}{1 + (\alpha_{AB} - 1)x_A} \quad (1.4)$$

To analyse any separation process, it is necessary to have an equilibrium equation, and deriving this is often the first step of a solution. 1.1 can be further exploited for ideal systems by combining with Raoult's Law:

$$y_A P = x_A P_A^*(T) \quad (1.5)$$

where  $P$  is the total pressure of the system, and  $P_A^*(T)$  is the vapour pressure of component  $A$ . Combining 1.5 and 1.1 we get

$$\alpha_{AB} \approx \frac{P_A^*(T)}{P_B^*(T)} \quad (1.6)$$

Therefore, the relative volatility  $\alpha_{AB}$  can be approximated as the ratio of the vapor pressures of the components. To solve a system involving ideal vapour-liquid equilibrium given  $x_A$ , first use the vapour pressures to approximate  $\alpha_{AB}$  using 1.6, then solve for  $y_A$  using 1.4.

## Gibbs Phase Rule and Two Phase Systems

All of the separations we will be studying in this class are two phase systems with two components. This means that there are exactly two components interacting with each other at any given

time, and these components are in no more than two phases, ie. liquid and vapour. Separations processes with these conditions are called *binary*.

We know if we have enough information to solve a given problem by analysing the *Degrees of Freedom* of a problem. Normally, this is understood as

$$\# \text{Equations} - \# \text{Knowns} = \text{Degrees of Freedom}$$

however there exists a special case called *Gibbs Phase Rule* which states

$$\text{Degrees of Freedom} = C - P + 2 \tag{1.7}$$

where  $C$  is the number of components or chemical species within the system as  $P$  is the number of phases within the system. Solving for our binary systems, we find that there are 2 Gibbs Degrees of Freedom for a binary separation. Gibbs Degrees of Freedom describe how many *intensive properties* are needed to define any given system.

**Definition.** *An intensive property is a property of the system that does not depend on the size of the system*

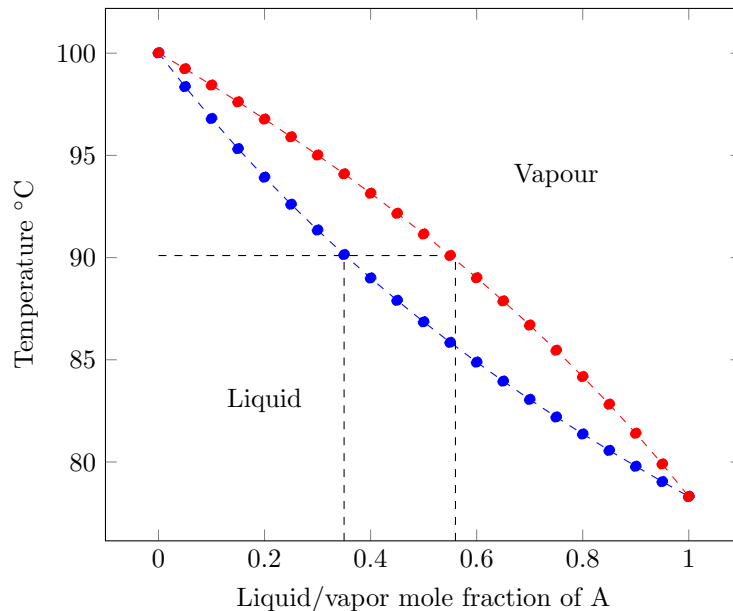
Common examples of intensive properties are *temperature, pressure, reflux ratio, and component fractions*. Other properties such as flow-rates are *extensive properties*, and are not accounted for by Gibbs Degrees of Freedom.

**Key Point.** *By Gibbs Phase Rule, a binary separation is defined by two intensive properties*

## Txy and x-y Plots

Equilibrium information comes in many forms. Often, it is defined by an equation, solved as we have seen previously from vapor pressure information. However, the most reliable source of equilibrium information is empirical data, which needs to be analysed graphically. Additionally, it serves quite useful to graph equilibrium expressions in separation process analysis. There are two main styles of graphical equilibrium information, *Txy* plots and *x-y* plots. Below is an example of a *Txy* plot, where component A is ethanol, and component B is water.

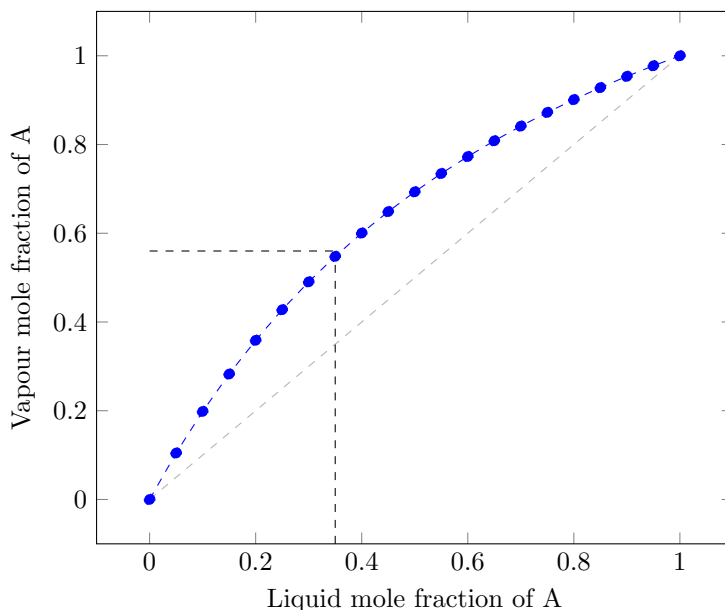
Figure 1.1: Txy Diagram for A and B



In this example, the bubble line is represented by the blue line, and the dew line is represented by the red line. This diagram represents equilibrium states across different temperatures, as every pair of points at the same temperature represents an instance of vapour-liquid equilibrium. For example, the above Txy plot highlights the equilibrium composition of  $x_A \approx 0.35$  and  $y_A \approx 0.55$  which occurs at  $90^\circ\text{C}$ . The line drawn between the two curves is called the *tie line* and this method of analysis is called the lever rule.

Similarly, these different equilibrium states can be plotted against each other, rather than temperature. This is a lossy process, *you can generate an x-y plot from a Txy plot, but you cannot generate a Txy plot from an x-y plot*, however, x-y plots enable useful analysis techniques which will be necessary to solve more complicated separation processes. Below is the same equilibrium information as above expressed in an x-y plot.

Figure 1.2: x-y Diagram for A and B



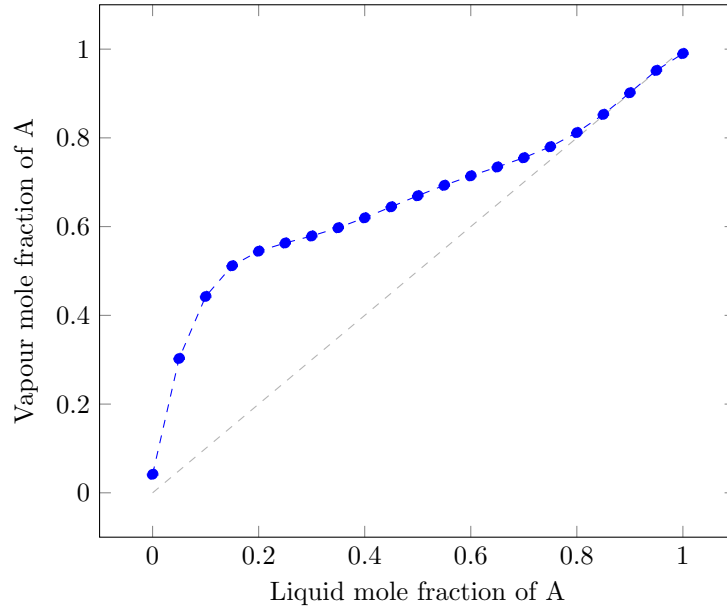
Note how the point  $(x_A, y_A)$ , which were on opposite sides of the tie line on the Txy plot, are now a point on the blue equilibrium line. Now each point on the graph represents an equilibrium state at some temperature. With these plots, it is often useful to plot the line  $y = x$  which is represented in grey. Think back to equation 1.4, the equilibrium expression form of relative volatility

$$y_A = \frac{x_A \alpha_{AB}}{1 + (\alpha_{AB} - 1)x_A}$$

Equations like this one are the blue line on this x-y plot! For this reason, almost all graphical analysis which aims to relate a separation process to equilibrium, will make use of this graph.

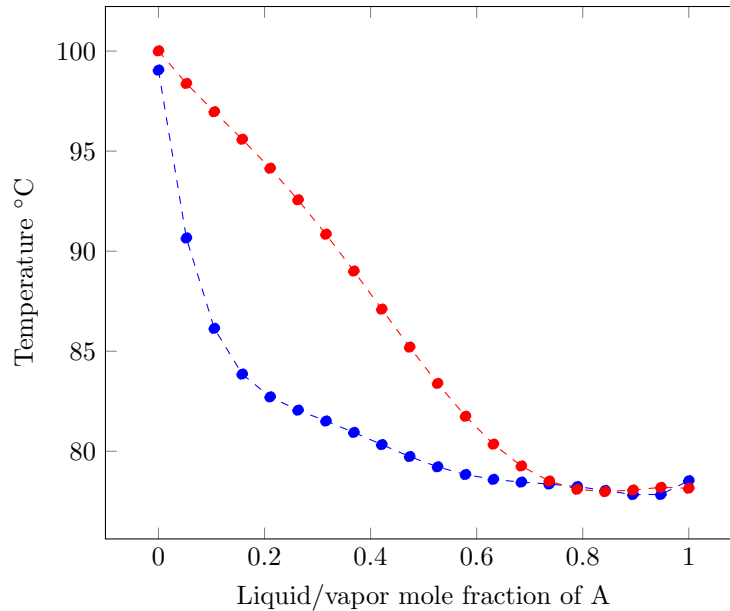
The above x-y diagram is an example of ideal VLE, the assumption which guides most mathematical analysis of volatility based separation processes. However, ideal equilibrium information is frequently quite different from information derived from imperial data, or even more complicated models. Here is an x-y plot of the equilibrium between the same two components, using the SRK equations of state.

Figure 1.3: x-y Diagram with Wilson Equation



Notice how it's not even the same shape! Non-ideal models and especially empirical data are significantly more accurate than ideal models. In this case, an azeotrope at  $x_A = y_A = 0.8$  is omitted from the ideal model. This is more clearly seen from the associated Txy diagram.

Figure 1.4: Txy Diagram with Wilson Equation



The intersection of the liquid mole fraction  $x$  and the vapour mole fraction  $y$  is the temperature when this mixture is an azeotrope.

**Definition.** An azeotrope is a solution in which the solution has a single uniform boiling point when liquid and mole fractions of a component are equal



Understanding when and if azeotropes occur is essential, as distillation of an azeotrope is not possible. Ideal models can never account an azeotrope, which is an example of how complex models and empirical data are always better than ideal models.

## Flash Distillation

We now have the tools to analyse our first unit operation. Flash distillation is by far the most straight forward of all the separation processes. A feed stream is fed into a flash drum, at which point it is instantaneously and continuously brought to a given temperature and pressure. The feed reaches equilibrium inside the drum, and then exits in a vapour and liquid product. As such, the more volatile component is of higher concentration in the vapour product. There is only one equilibrium stage. For all separations based on volatility, the relative volatility of the two components must be sufficiently high such that the following inequality is satisfied

$$\alpha_{AB} \geq 1.05 \tag{1.8}$$

### Quick Facts.

- *Property Exploited: Volatility*
- *Driving Force: Vapour-Liquid Equilibrium*
- *Separation: Vapour/Liquid*

The property exploited is the property of the components that is the basis for the separation. The driving force is the aspect of the system that causes the separation. Although in this case they are for all intents and purposes the same, this isn't necessarily true, as we will see in later sections. Below is a *Process Flow Diagram*, or PFD of a flash distillation.

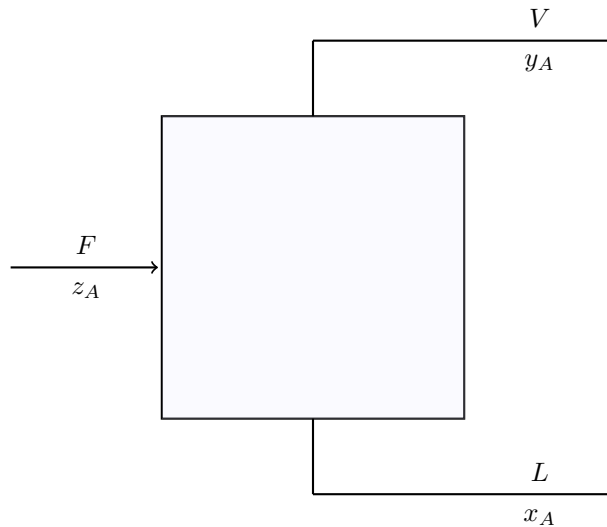


Figure 1.5: PFD of Flash Drum

In this diagram  $F$ ,  $V$ , and  $L$  are the *Feed*, *Vapour*, and *Liquid* flowrates respectively, and would be measured in units such as  $kgmol/h$  or  $lb/min$ .  $z_A$ ,  $y_A$ , and  $x_A$  are the overall, vapour, and liquid fraction of  $A$ , in their respective streams.

As for all separation processes, we know that the amount of mass or moles of feed flowing into the system is equal to the amount of product leaving the system. Therefore, two mass balances can be derived around this flash drum:

$$F = V + L \quad (1.9)$$

$$Fz_A = Vy_A + Lx_A \quad (1.10)$$

1.9 describes the overall mass balance of the system, while 1.10 is the mass balance with respect to component  $A$ . Solutions to flash drums frequently involve combining these two equations. If, during the solution process, these mass balances result in a contradiction, the distillation in question is not achievable with this method.

It is quite commonplace, particularly with more intricate processes, for the subscript  $A$  to be dropped, as it is implied that in a binary system, we are referring to the composition of the more volatile component. These variables,  $z_A$ ,  $y_A$ ,  $x_A$  are what we call *mole fractions*. As you may recall, they represent the fraction of component  $A$  in each particular stream. Although these are generally expressed as unitless quantities, there is a nuance to the units themselves. The units of  $x_A$ , for example are:

$$\frac{\text{moles of liquid } A}{\text{total moles of liquid}}$$

which we can further simplify to

$$\frac{\text{mol } A}{\text{mol}}$$

and is generally thought of and canceled out as "moles per mole". While you may never explicitly express the units of these mole fractions, and simplify these variables to unitless quantities, be sure to keep in mind that, for example, the units of  $x_A$  and the units of  $y_A$  are different as they are fundamentally not measuring the same thing.

When solving any separation process, it is essential to make key assumption which enable certain methods of analysis. The assumptions for flash distillation are as follows

1. Continuous Process at Steady State
2. No Reactions
3. Ideal Vapour-Liquid Equilibrium

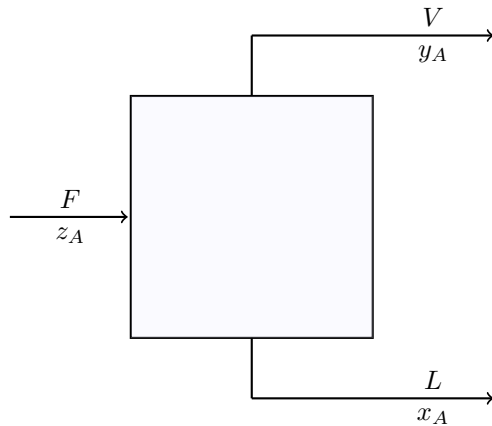
It is essential to include these assumptions in any solution to a flash distillation. The assumption of steady state and continuous allows us to treat the flowrates as constant, and the assumption of no reactions enables us to draw the partial mass balance of 1.10. Assuming ideal equilibrium lets us apply Raoult's law, 1.5, and all other equations which only apply in an ideal setting.

There is a very similar process to flash distillation which involves stacking multiple flash drums in series to create multiple equilibrium stages. Condensers placed after intermediate vapour streams to ensure vapour-liquid interaction occurs. This is called a *Flash Drum Cascade*. It will be left as an exercise to the reader to extend our model of process analysis to flash drum cascades.

## Chapter Review : Equilibrium and Two-Phase Systems

In this chapter, we learned about vapour-liquid equilibrium, what equilibrium is, and how to use graphical and algebraic equilibrium information to solve a problem. Then, we learned our first application of a separation process, flash distillation, which exploits volatility and is driven by VLE.

### Flash Distillation PFD



### Flash Distillation Assumptions

1. Continuous Process at Steady State
2. No Reactions
3. Ideal Vapour-Liquid Equilibrium

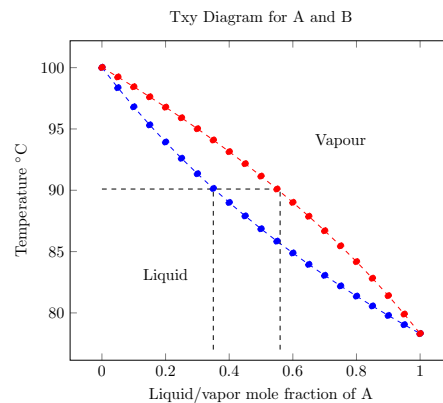
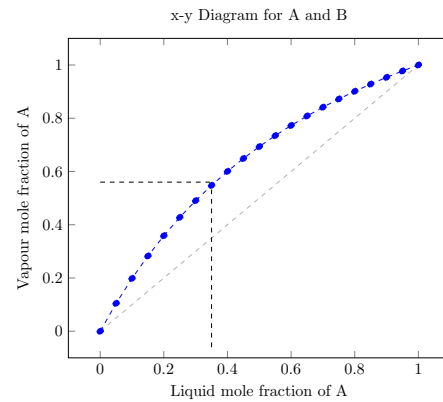
### Equations

1.  $\alpha_{AB} = \frac{P_A/x_A}{P_B/x_B} \geq 1$
2.  $\alpha_{AB} = \frac{y_A/x_A}{y_B/x_B}$
3.  $y_A = \frac{x_A \alpha_{AB}}{1 + (\alpha_{AB} - 1)x_A}$
4.  $\alpha_{AB} \approx \frac{P_A^*(T)}{P_B^*(T)}$
5.  $\alpha_{AB} \geq 1.05$
6.  $P_A = y_A P$
7.  $y_A P = x_A P_A^*(T)$
8. Degrees of Freedom =  $C - P + 2$
9.  $F = V + L$
10.  $Fz_A = Vy_A + Lx_A$

**1-4.** Equations for relative humidity **5.** Inequality for distillation **6.** Partial Pressure **7.** Raoult's Law **8.** Gibbs Phase Rule **9-10.** Mass balance for flash drum

### Txy and x-y diagrams

Equilibrium information can be read of Txy and x-y diagrams as shown in these figures



### Key Points

- The best equilibrium information is empirical data
- Intensive properties are size-independent
- Binary systems have two Gibbs Degrees of Freedom
- Azeotropes occur when  $x_A = y_A$  and cannot be distilled

# Chapter 2

## Column Distillation

Suppose you wish to perform a separation which requires ten equilibrium stages to complete, five to purify the vapour product, and five to purify the liquid product. With flash drums, this would require ten of them, stacked in series. The facility required to house this equipment would be enormous and the cost would be prohibitive. Fortunately, there is a better way.

### The Stripping Column

In order to spend an entire semester discussing separation processes, one must truly fall in love with distillation columns. One must study them during the day and dream of them at night. One must let them become every breath, every word. One must become obsessed. Is it no wonder then, that here, with stripping columns, is where the journey begins?

A stripping column is a vapour/liquid separation unit which strips a liquid feed of the more volatile component. It is a multi-stage process, with different equilibria occurring at different temperatures at different discrete trays throughout the column.

#### Quick Facts.

- *Property Exploited: Volatility*
- *Driving Force: Vapour-Liquid Equilibrium*
- *Separation: Vapour/Liquid*

The column itself is made up of individual trays, which allow vapour and liquid phases to interact. Each tray has a unique equilibrium composition, hence, this is a multi-stage process. This is leveraged to create a much more powerful separation process than a single-stage flash drum.

The trays themselves are made up of large circular disks with bubbling areas welded to them, separated from the walls of the column by barriers called *weirs* which extend above the tray. Liquid interacts with vapour at these bubbling areas, and excess will overflow into the tray below via the bottom part of the weir called the *downcomer*. Similarly, vapour will rise above to the next tray.

Below is the PFD of a stripping column:

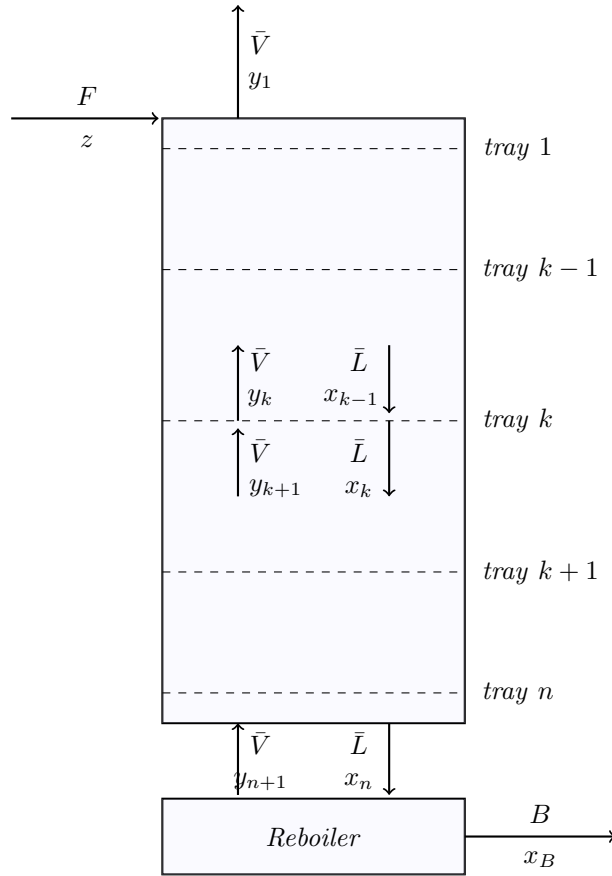


Figure 2.1: PFD of Stripping Column

In this diagram,  $z$  refers to the feed composition, each  $y_k$  and  $x_k$  refer to the vapour and liquid compositions of their respective stream,  $\bar{V}$  and  $\bar{L}$  are the vapour and liquid streams, where the bar drawn above the variable signifies that this is a stripping column.  $B$  represents the bottoms product stream and  $F$  represents the feed stream. By convention, trays are numbered top down, with tray  $n$  being the last tray on the bottom and streams are numbered with respect to the tray which they are leaving, Arbitrary trays in a stripping column are denoted with the letter  $k$ .

It is important to recognise the difference between stages and trays.

**Definition.** *An equilibrium stage is a place in which there exists equilibrium between the two components*

At first it may seem as if stages and trays mean the same thing, after all, trays are stages. However, trays are not the only place within a stripping column in which equilibrium occurs. Consider the reboiler; within the reboiler, there is a liquid input and both a vapour and liquid output, therefore the reboiler is an equilibrium stage. Note that this is true only in the case of a *partial* reboiler, one which does not reboil the entire stream. For total heat exchangers, modules in which the phase of the entire feed is changed, no equilibrium occurs, and thus they are not stages.

Just as in flash distillation, stripping columns come with their own set of assumptions, most of which should be familiar. The standard set of assumptions are as follows

1. Constant Molar Overflow (CMO)
2. Constant Pressure

3. Ideal Stages
4. Continuous Process at Steady State
5. No Reaction

We must assume that the system is at constant pressure, as pressure will also affect each equilibrium stage differently. We also make a new assumption, called *Constant Molar Overflow*, often abbreviated as CMO.

**Definition.** *Constant Molar Overflow is the assumption which claims that the moles of vapour and liquid which flow from one tray to the next are constant throughout the column*

The implication of CMO is that we can assume

$$\bar{V}_1 = \bar{V}_2 = \bar{V}_3 = \dots = \bar{V}_n$$

and

$$\bar{L}_1 = \bar{L}_2 = \bar{L}_3 = \dots = \bar{L}_n$$

in other words, that any liquid and vapour flows are equal to each other. Note that:

$$\bar{L}_k \neq \bar{V}_k$$

The equality only holds between vapour and liquid flows respectively. This is why in the diagram, rather than labeling the flowrates  $\bar{V}_1, \bar{V}_2, \bar{V}_3 \dots$ , instead they are all simply labeled  $\bar{V}$ .

The following mass balances can be drawn around a stripping column.

$$F = \bar{V} + B \tag{2.1}$$

$$\bar{L} = \bar{V} + B \tag{2.2}$$

$$\bar{L}x_{k-1} = \bar{V}y_k + Bx_B \tag{2.3}$$

Through combining equations 2.1 and 2.2, a key understanding is reached about stripping columns:  $F = \bar{L}$ . Although this may be surprising at first, in the context of a stripping column, it should make sense. Suppose a stripping column had a mixed vapour-liquid feed. All vapour in this feed would immediately flow out in  $\bar{V}_1$ . Thus stripping columns only take a liquid feed, all of which enters the first tray. By assuming CMO, if one of the liquid flowrates is equal to the feed flowrate, all of them must be. Therefore, in a stripping column,  $F = \bar{L}$ .

Although many possible partial balances can be drawn all throughout the column, 2.3 is of particular importance. Rearranging variables, we get the following:

$$y_k = \frac{\bar{L}}{\bar{V}}x_{k-1} - \frac{B}{\bar{V}}x_B \tag{2.4}$$

Which is a line, with slope and intercept:

$$\frac{\bar{L}}{\bar{V}} \quad \text{and} \quad -\frac{B}{\bar{V}}x_B$$

## The Operating Line: Stripping

We will now discuss the operating line of a separation process, as it applies to stripping columns. For all multi-stage separation processes with discrete stages, an operating line can be derived from the partial mass balance around these stages. Whereas the equilibrium line, which is plotted on an x-y plot, shows the relationship between an  $y_k$  and  $x_k$  in equilibrium, the operating line shows the relationship between  $y_k$  and  $x_{k-1}$ . Physically on a stripping column, this represents the composition of the streams entering and leaving a tray on the same side.

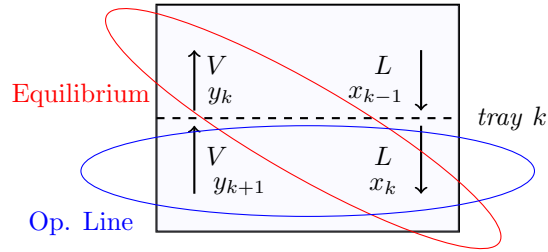


Figure 2.2

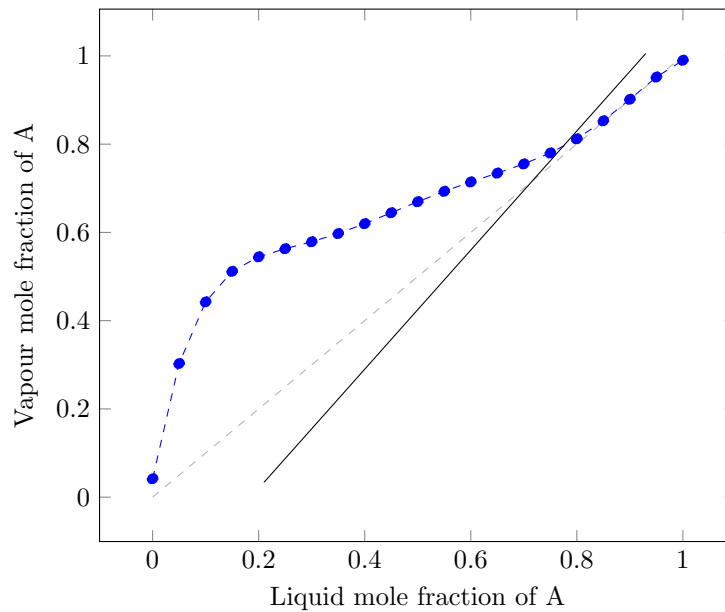
Here we can see the physical relationship between the equilibrium line and the operating line with respect to any given tray on a stripping column.

As derived in the last section 2.4, the operating line of a stripping is

$$y_k = \frac{\bar{L}}{\bar{V}} x_{k-1} - \frac{B}{\bar{V}} x_B \quad (2.4)$$

which can be plotted alongside an equilibrium line on an x-y plot as seen below. This is the Wilson Equation model for vapour-liquid equilibrium between ethanol and water from Chapter 1. Note that the equilibrium line contains all points  $(x_k, y_k)$ , and the operating line contains all points  $(x_{k-1}, y_k)$ .

Figure 2.3: Equilibrium Line and Operating Line



We can determine much about this process from this stripping line. The points of intersection with the equilibrium line are the bounds of the stripping process, ie. it would be impossible to process a feed stream with  $0x > 0.5$  or  $x < 0.1$ . Secondly, we know that the slope of the operating line is equal to  $\bar{L}/\bar{V}$ , so we can further solve the system with this information. Lastly, as an exercise, substitute  $x_B$  for  $x$ . You will discover that the point  $(x_B, x_B)$  always exists on the stripping operating line. Since this gives you both a point and a slope, this information is particularly useful when drawing the operating line.

You may have also noticed that this line has a negative  $y$ -intercept and a slope greater than one. In a stripping column it is always true that

$$\frac{\bar{L}}{\bar{V}} \geq 1$$

This has large implications for boilup, the ratio of  $\bar{V}/B$ , as this limits the possible boilup ratios for a given system.

**Key Point.** *The case of maximum boilup corresponds to the minimum slope of the operating line which is the line  $y = x$*

Conversely, the maximum boilup possible is represented by the operating line drawn between the points  $(x_B, x_B)$  and  $(z, y^*)$  where  $y^*$  is the vapour concentration in equilibrium with the liquid feed.

Boilup is a key factor in a stripping column, and oftentimes it is one of the intensive properties needed to solve a system. Given this, it is possible to express the operating line for a stripping line in terms of the boilup ratio,  $R_B$ . This is derived in Appendix A from 2.4 and the definition of the boilup ratio as  $\bar{V}/B$ .

$$y_k = \frac{R_B + 1}{R_B} x_{k-1} - \frac{1}{R_B} x_B \quad (2.5)$$

## McCabe-Thiele Analysis: Stripping

We now have all the information we need to leverage McCabe-Thiele analysis to determine how many equilibrium stages are necessary to complete a stripping distillation.

We are going to draw a staircase from the feed stream composition, all the way down to the bottoms product composition, placing a stair at every equilibrium stage. Conceptually, these stairs represent first traveling from the vapour composition leaving a tray to the liquid composition leaving the tray, then from the liquid composition leaving the tray to the vapour composition entering the tray, leveraging the equilibrium and operating lines respectively.

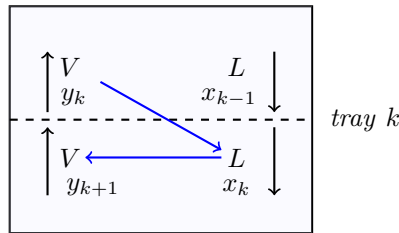
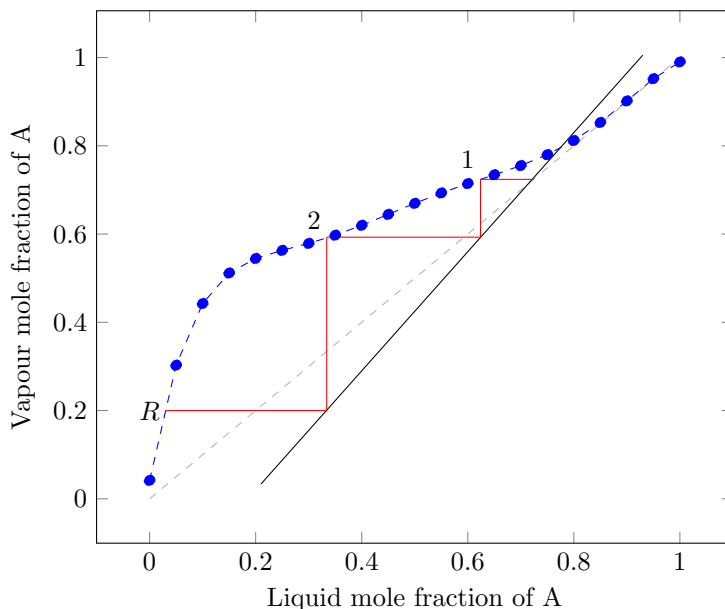


Figure 2.4 McCabe-Thiele, Actually

Here, the line from  $y_k$  to  $x_k$  represents the first part of the stair, and the line from  $x_k$  to  $y_{k+1}$  represents the second part of the stair. Let's see the stairs on an actual  $x$ - $y$  plot.



Figure 2.5: Example of McCabe-Thiele Analysis



Now we can see the stairs in all their glory. The horizontal part of the stairs move from  $y_k$  to  $x_k$  and the vertical part of the stairs move from  $x_k$  to  $y_{k+1}$ . This example is for a stripping column whose feed is  $z = 0.8$  and whose bottoms product is  $x_B = 0.03$ . These compositions are the top and bottom of the staircase. Each stair represents an equilibrium stage, meaning this process would require 3; two trays and one partial reboiler. The stages are labeled top from bottom, and the bottom stage is labeled *R* for *Reboiler*. Note that you cannot do McCabe-Thiele analysis when the operating line is above the equilibrium line. This is a general heuristic for the limiting conditions of operating lines - if McCabe-Thiele analysis is geometrically prohibited, the separation is not feasible.

When drawing McCabe-Thiele analysis on a physical graph, it is important to be as accurate as possible. For this reason, always use a straight-edge and begin drawing lines from the target composition at the bottom of the column.

In the last section we learned that when the operating line is  $y = x$ , the boilup ratio is maximised. But what happens to the number of stages? It should be rather easy to infer graphically, that as the line becomes steeper, the number of stairs on the McCabe-Thiele staircase increase.

**Key Point.** *The steepest operating line corresponds to the maximum number of stages,  $n = \infty$  and the operating line  $y = x$  corresponds to the least possible number of stages (maximum boilup)*

## The Enriching Column

What if you would like to increase the composition of the more volatile component via distillation? If so, an enriching column is the separation process best suited for your needs.

An enriching column is a vapour/liquid separation unit which enriches a vapour feed with the more volatile component, producing a vapour product which is condensed into a liquid distillate. It is a multi-stage process, and as you will see, is quite analogous to stripping columns.

### Quick Facts.

- *Property Exploited: Volatility*

- Driving Force: Vapour-Liquid Equilibrium
- Separation: Vapour/Liquid

Enriching columns are constructed in the same manner as stripping columns, the key difference being that the feed is placed at the bottom rather than at the top. Below is a PFD of an enriching column.

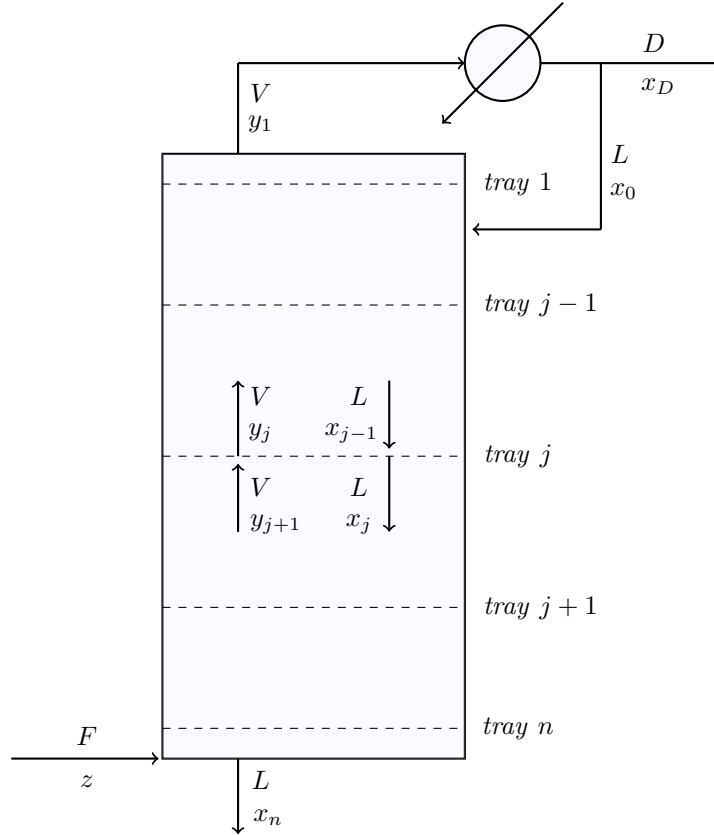


Figure 2.6: PFD of Enriching Column

For enriching columns, the bar is dropped above all flowrates, and arbitrary trays are denoted as  $j$ . Above the column is a total condenser, which processes the vapour outlet  $V_1$  and condenses it into a liquid. Of this liquid, some is produced as distillate product  $D$ , and the remainder is fed back into the column as reflux,  $L_0$ . Reflux is the enriching equivalent of boilup.

While typically an enriching column will have a total condenser, it is possible for an enriching column to have a partial condenser. Similar to a partial reboiler, a partial condenser has both vapour and liquid streams leaving the heat exchanger. In this case, there is a vapour purge as well as the distillate product stream as shown below.

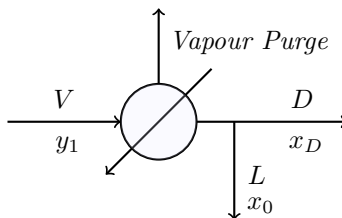


Figure 2.7: PFD of Partial Condenser

The assumptions for enriching columns are the same as the assumptions for stripping columns:

1. Constant Molar Overflow (CMO)
2. Constant Pressure
3. Ideal Stages
4. Continuous Process at Steady State
5. No Reaction

And in a similar way to stripping columns, mass balances can be drawn around the trays, condenser, and entire column.

$$F = L + D \tag{2.6}$$

$$V = L + D \tag{2.7}$$

$$Vx_{j+1} = Ly_j + Dx_D \tag{2.8}$$

By combining equations 2.6 and 2.7, we can clearly see that  $F = V$  in the same way that  $F = \bar{L}$ . This should make sense conceptually, as any liquid feed will simply flow out the bottom of the column. Also, by rearranging equation 2.8 we get the operating line for an enriching column.

$$y_j = \frac{L}{V}x_{j-1} + \frac{D}{V}x_D \tag{2.9}$$

## The Operating Line: Enriching

There are a few key differences between the operating line for a stripping column. A helpful heuristic for understanding this is that enriching tends to be opposite in chirality from stripping. The first difference is the equation itself:

$$y_k = \frac{\bar{L}}{V}x_{k-1} - \frac{B}{V}x_B \tag{2.4}$$

$$y_j = \frac{L}{V}x_{j-1} + \frac{D}{V}x_D \tag{2.9}$$

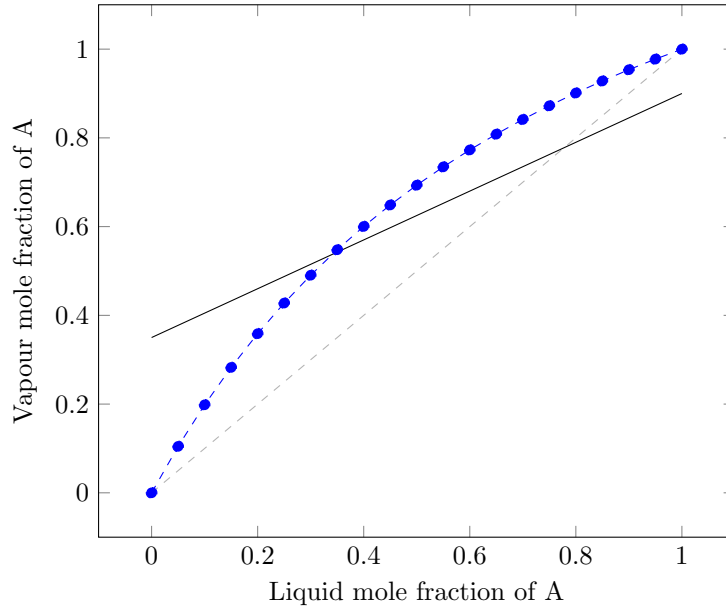
Although the variables are roughly in the same place, these two lines behave somewhat differently. The cause for this is the relationship between the feed stream  $F$  and the vapour or liquid stream  $V$  and  $\bar{L}$ . In stripping columns, the feed flowrate is equal to the numerator of the operating line slope. In enriching columns, the feed flowrate is equal denominator of the operating line slope.

Another manifestation of this mirror-image relationship is the reflux form of the equation for the operating line. The reflux ratio is defined as  $R = L/D$ , the proportion of vapour product condensed and fed back into the column as opposed to extracted as product. Combining this with the operating line, we get

$$y_j = \frac{R}{1+R}x_{j-1} + \frac{1}{1+R}x_D \tag{2.10}$$

which is quite similar to the operating line of a stripping column written in terms of the boilup ratio. This is also proven in Appendix A. Graphically, they are similar but different as well.

Figure 2.8: Operating Line for Enriching



Notice how now, the operating line has a slope lesser than one, intersecting the  $y$ -axis above the  $x$ -axis. It is indeed true that  $0 \leq L/V \leq 1$ , and again, this returns to the numerator-denominator relationship between stripping and enriching operating lines and their feed.

What then, do you think happens in the case of minimum reflux? Since  $F = V$ ,  $L$  increases as reflux increases (Remember that all liquid and vapour flows are constant throughout the column by CMO). This should be evident from the PFD of an enriching column. But, we know that  $L/V \leq 1$ , since the slope of the operating line is more shallow than  $y = x$ . Conceptually, this represents that  $L < V = F$ . If  $L$  were to exceed  $V$  and  $F$  then somehow your column would be generating mass, a discovery worth further investment. Thus, maximum reflux is when  $L$  is maximised, when  $L = V$ , and minimum reflux is when  $L$  is minimised.

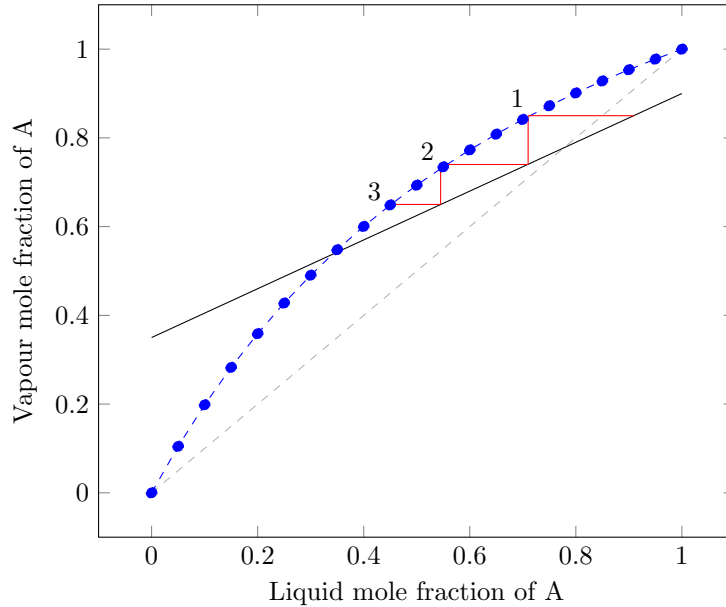
**Key Point.** *The shallowest operating line corresponds to the maximum number of stages,  $n = \infty$  (minimum reflux), and the operating line  $y = x$  corresponds to the least possible number of stages (maximum reflux  $R = 1$ )*

To draw the operating line which represents the case of minimum reflux, begin at the point  $(x_D, x_D)$ , a point which we know is on the enriching operating line for the same reason that the point  $(x_B, x_B)$  is on the stripping operating line. Then, find the point on the equilibrium line where  $y^* = z$ , which we can notate as  $(x^*, z)$ . Notice how now the  $z$  term represents a  $y$ -coordinate, whereas in stripping,  $z$  represents an  $x$ -coordinate. This is because enriching columns require a vapour feed, while stripping columns require a liquid feed. The line drawn between  $(x_D, x_D)$  and  $(x^*, z)$  will be the operating line of shallowest slope for the separation in question, and will represent the case of minimum reflux. For example, the operating line drawn in Figure 2.8 represents the case of minimum reflux for a column whose feed has the composition  $z \approx 0.5$ .

## McCabe-Thiele Analysis: Enriching

For those who have mastered the art of McCabe-Thiele Analysis for a stripping column, applying the technique to an enriching column should come with relative ease. It is after all, the same process, which requires the same conceptual understanding. Here, we begin at the point  $(x_D, x_D)$  and draw our stairs down towards the feed, represented by the point  $(x^*, z)$ . Just as before, the number of stages is represented by the number of stairs drawn on the graph.

Figure 2.9: McCabe-Thiele Analysis for Enriching



From this plot, we can see that an enriching process, which enriches a vapour feed of  $z = 0.65$  to a purity of  $y = 0.85$ , requires three equilibrium stages, labeled as three trays. Why, you may ask, isn't the condenser considered one of the stages? If it were a partial condenser, then it would be correct to label what is labeled *1* on Figure 2.9 *C* for condenser, but as there is typically a total condenser in an enriching column, and total heat exchangers are not equilibrium stages, it is safe to say that this process requires three trays.

Once more, we can understand the limits of our unit operation through the geometric limits of McCabe-Thiele analysis. We cannot enrich feeds more dilute than where the operating line intersects the equilibrium line, and approaching this point would require exponentially more trays as we get nearer. Observations such as these are why graphical McCabe-Thiele analysis is such a powerful tool.

## Tray Column Distillation

When the feed stream is placed at the bottom of a tray column, the result is an enriching column, and when the feed stream is placed at the top of a tray column, the result is a stripping column. But what if the feed is placed somewhere in between?

In that case, we have a standard tray column. The area above the feed is the *enriching section* and the area below the feed is the *stripping section*. Both operate exactly as we have learned, but there are some novel consequences to putting them together. The best way to understand what is happening is by looking at a PFD.

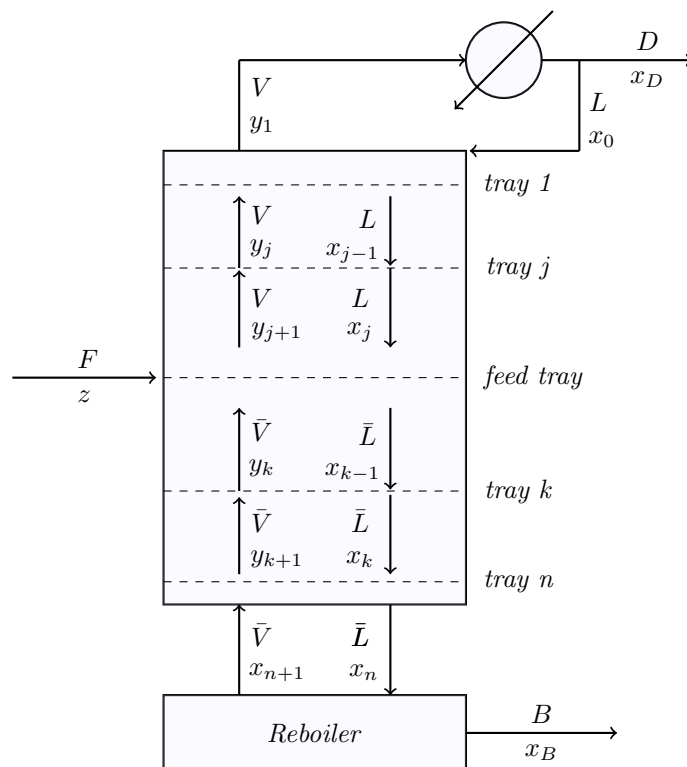


Figure 2.10: PFD of Tray Column

Notice how this is simply an enriching column and a stripping column put on top of one another! The motivation for this is simple: where each section can only process a single-phase feed, a tray column can process a mixed feed, producing both stripped and mixed products. Often, multiple organic compounds are produced simultaneously, all valuable in their pure form. As such, a tray column can separate and purify both the more and less volatile compound.

#### Quick Facts.

- *Property Exploited: Volatility*
- *Driving Force: Vapour-Liquid Equilibrium*
- *Separation: Vapour/Liquid*

It should come as no shock that the property exploited, driving force, and separation environment are the same for enriching columns, stripping columns, and overall tray distillation. As a rule, what is true for enriching and stripping columns is true for the enriching and stripping sections of a tray column. For example, these are the assumptions for a tray column.

1. Constant Molar Overflow (CMO)
2. Constant Pressure
3. Ideal Stages
4. Continuous Process at Steady State
5. No Reaction

What does CMO mean for a tray column? The implication is slightly different from stripping and enriching columns. Within each section, stripping and enriching, all  $V = V$  and all  $L = L$ , however, this is not true across sections. Importantly,

$$\bar{V} \neq V$$

$$\bar{L} \neq L$$

The vapour part of the feed is equal to  $V$  and the liquid part of the feed is equal to  $\bar{L}$ , otherwise stated as

$$F = V + \bar{L} \quad (2.11)$$

which is easily derived as the mass balance around the feed tray. Similarly, the overall and partial mass balances of a tray column are

$$F = B + D \quad (2.12)$$

$$Fz = Bx_B + Dx_D \quad (2.13)$$

Note that 2.12 and 2.13 can be rearranged as

$$D = \left( \frac{z - x_B}{x_D - x_B} \right) F \quad (2.14)$$

The operating lines, derived from the partial mass balances drawn around arbitrary *tray j* and *tray k* remain the same. Note that a tray column does not have one operating line, but two, which is another implication of CMO for tray columns.

$$y_k = \frac{\bar{L}}{\bar{V}}x_{k-1} - \frac{B}{\bar{V}}x_B \quad (2.4)$$

$$y_j = \frac{L}{V}x_{j-1} + \frac{D}{V}x_D \quad (2.9)$$

The boilup and reflux ratios are also important intensive properties of a tray column, where

$$R_B = \frac{\bar{V}}{B} \quad (2.15)$$

$$R = \frac{L}{D} \quad (2.16)$$

and the operating lines of each section can be rewritten in terms of these ratios

$$y_k = \frac{R_B + 1}{R_B}x_{k-1} - \frac{1}{R_B}x_B \quad (2.5)$$

$$y_j = \frac{R}{R + 1}x_{j-1} + \frac{1}{R + 1}x_D \quad (2.10)$$

## The Feed Line

Since the feed is no longer restricted to a single phase, it is useful to the analysis of a tray column to quantitatively capture the liquid-like and vapour-like nature of the feed.

**Definition.** *The quality of the feed  $q$  is the fraction of the feed which is liquid*

Feed quality  $q$  is defined by the following

$$q = \frac{\bar{L} - L}{F} \quad (2.17)$$

$$1 - q = \frac{V - \bar{V}}{F} \quad (2.18)$$

It will be left as an exercise to the reader to derive 2.18 from 2.17.

Leveraging these definitions of  $q$ , and the partial mass balances for the feed tray with respect to each section (*note that these already contain the substitution of  $V$  and  $\bar{L}$  for  $F$* )

$$Vy = Lx + Dx_D$$

$$\bar{V}y = \bar{L}x - Bx_B$$

a very important line, called the  $q$ -line or feed line, can be derived which enables full McCabe-Thiele analysis for a tray column. The derivation of this is in Appendix A.

$$y = \frac{q}{q-1}x + \frac{z}{1-q} \quad (2.19)$$

Since 2.19 is derived from the assumption that  $y_j = y_k$  and  $x_j = x_k$ , it necessarily describes the feed stage, which is the exact use case we will see shortly. In the same way that the point  $(x_B, x_B)$  will always lie on the stripping operating line, the point  $(z, z)$  will always lie on the feed line. Proving this will be left to the reader.

What kinds of feed quality are there? The most common type of feed is a mixed feed which contains both liquid and vapour. Saturated liquid feeds and saturated vapour feeds contain only liquid and vapour, and are at the bubble and dew points respectively. Lastly, subcooled and superheated feeds are liquid and vapour feeds at extreme temperatures.

**Definition.** *A superheated vapour cannot be condensed at any pressure*

**Definition.** *A subcooled liquid is a liquid below the saturation temperature*

Superheated and subcooled feeds cause strange behaviors with respect to the liquid and vapour streams. This is because the temperature of the feed affects the temperature of the column itself. For example, a subcooled liquid feed can condense the vapour flow  $\bar{V}$  into liquid  $\bar{L}$ . Thus  $\bar{L} > L$  and  $q > 1$

All five feed types change  $q$  and create a  $q$ -line with unique properties. These have been tabulated below:

Feed Type	$q$ -value	$q$ -line slope	$y$ -intercept
Subcooled Liquid	$q > 1$	positive	negative
Saturated Liquid	$q = 1$	$x = z$	N/A
Mixed Feed	$0 < q < 1$	negative	positive
Saturated Vapour	$q = 0$	$y = z$	$z$
Superheated Vapour	$q < 0$	positive	positive

Figure 2.11  $q$ -value and  $q$ -line information

## McCabe-Thiele Analysis: Tray Columns

Think back to the derivation of the feed line and how it is defined. We leveraged the fact that the equilibrium composition of the feed tray is both part of the stripping and enriching section. This also tells us something about the operating lines:

**Key Point.** *The intersection of the enriching operating line and the stripping operating line occurs on the feed line*

When drawing these lines on an x-y plot, this is unimaginably important. For example, given a feed line, the points  $(x_D, x_D)$ ,  $(x_B, x_B)$ , and either operating line slope, both operating lines can be constructed. Remember, no matter how complex, a binary, two-phase system can be defined



completely from two intensive properties. The feed line is the key to realising this.

With an x-y plot of equilibrium information, the enriching and stripping operating lines, and the feed line, we are now ready to perform McCabe-Thiele analysis on a tray column.

Figure 2.12: Complete x-y plot for Tray Columns

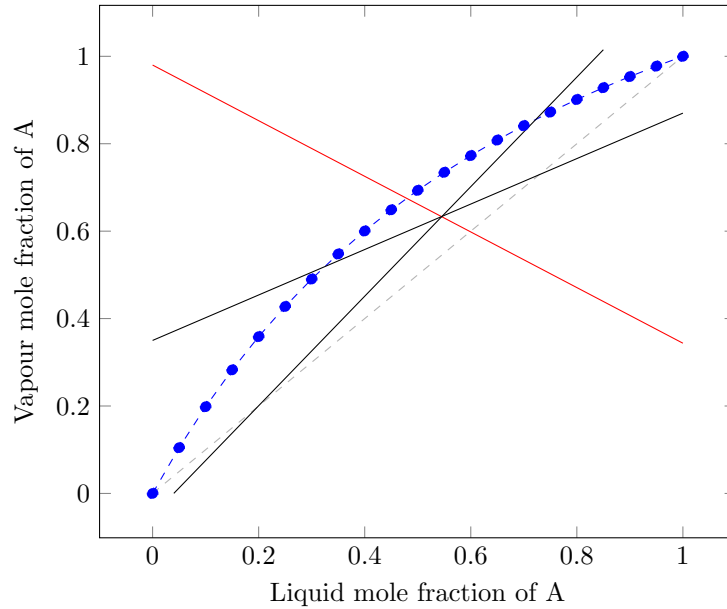
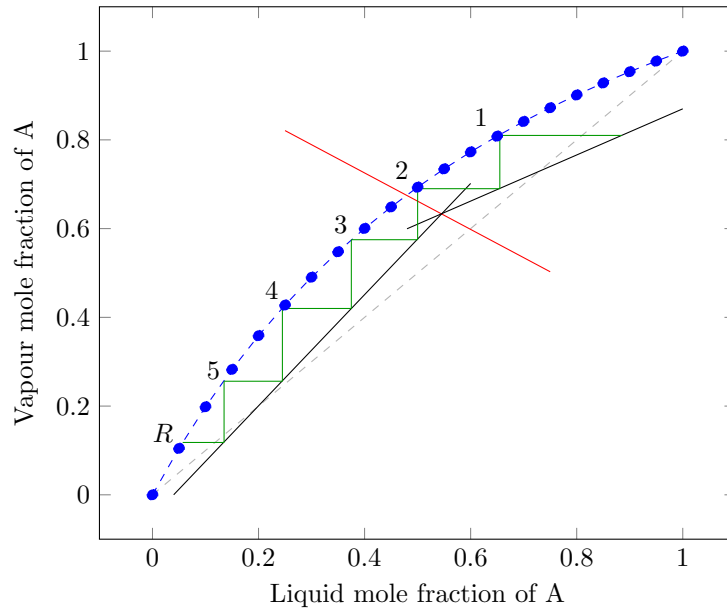


Figure 2.12 is an x-y equilibrium plot in blue, with the  $q$ -line in red, and enriching and stripping operating lines in black. Using the line  $y = x$  in grey, it is clear which line is the stripping operating line, and which line is the enriching operating line. During McCabe-Thiele analysis, the enriching operating line is only relevant above the intersection with the feed line, and the stripping operating line is only relevant below this point. Notice that the range of possible enriching operating lines is the set of lines which contain  $(x_D, x_D)$  and intersect the feed line between its intersection with the equilibrium line and the line  $y = x$ . The equivalent statement is also true of the stripping operating line and  $(x_D, x_D)$ .

Figure 2.13: McCabe-Thiele Analysis for Tray Columns



Above is an example of McCabe-Thiele analysis for a full tray column. The irrelevant sections of both operating lines have been shortened to make the diagram more visually clear. Analysis on a full column should generally begin on the side of the column for which you are given information. In this case, assume analysis begins at the top. Notice how after the analysis staircase crosses the feed line, the vertical lines are drawn to the stripping operating line, whereas before they are drawn to the enriching operating line. Although this seems logical, doing McCabe-Thiele analysis with respect to the wrong line is a very common error.

Also pay attention to how the sixth and final stage is labeled as the reboiler, yet the first stage is not labeled as the condenser. This is because a standard distillation column has a partial reboiler which is an equilibrium stage and a total condenser which is not. This column has six stages, five trays, and produces a distillate of  $x_D = 0.8$  and a bottoms product of  $x_B = 0.05$ .

What is the feed composition? Technically, the feed could be comprised of any composition, so long as it lies on the relevant operating line beneath the equilibrium line. However there is a correct choice.

**Key Point.** *The ideal feed stage is the stage which contains the intersection of the feed line and the equilibrium line.*

In Figure 2.13, the ideal feed stage would be tray 3. When drawing McCabe-Thiele analysis for a column with non-ideal feed placement, switch which operating line the vertical lines are drawn to once the *feed stage* is passed, not the intersection of the feed line and the equilibrium line. The latter method implies ideal feed placement.

The composition of each tray can also be determined from McCabe-Thiele analysis. The corner of each McCabe-Thiele stair which touches the equilibrium line at point  $(x_j, y_j)$ , where  $j$  is the number of the stage, counted from the top.

## Temperature and Pressure

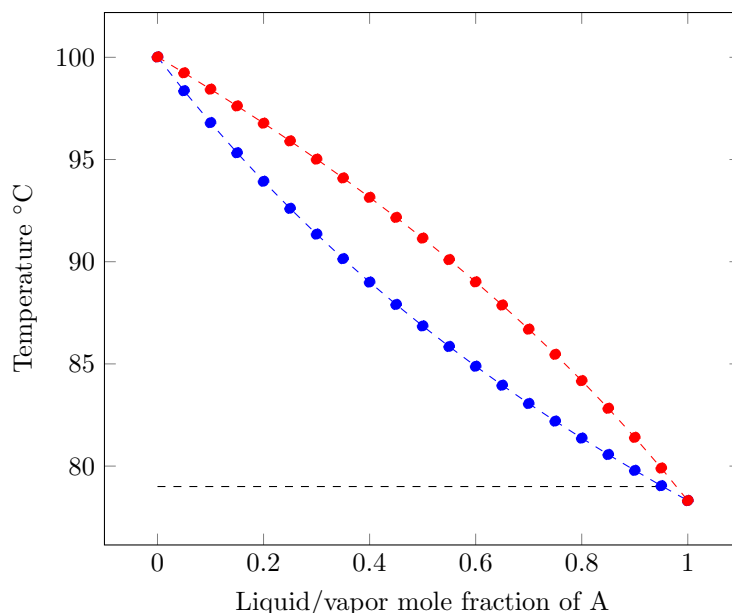
Reboilers are a heat exchanger which heats a liquid stream until it vaporises. A condenser is a heat exchanger which cools a vapour stream until it condenses. It then follows, that the warmest point on the column is the reboiler, and the coolest point on the column is the condenser. Through the rest of the column, the temperature varies, increasing down the column. We refer to the maximum and minimum temperatures of a column as  $T_{min}$  and  $T_{max}$  respectively.

This temperature trend should be logical, because, near the top of the column, the vapour stream contains mostly the more volatile component, which is to be expected at a lower temperature.

**Key Point.** For a condenser to operate cost-effectively,  $T_{min} \geq 30^\circ C$

This is because water cannot be used as a coolant for temperatures less than  $30^\circ C$ , and water is by far the most cost-effective coolant. Importantly, it is cheaper to change the pressure, than to utilize a different coolant.

Figure 2.14: Txy Diagram for A and B



Suppose the distillate product of a distillation column has the composition  $x_D = 0.95$ . What is the temperature  $T_{min}$ ? Determining this is fairly easy, simply find the isothermic line on the Txy plot which represents this composition and determine the temperature. For a composition of  $x = 0.95$ , the temperature must be  $79^\circ C$ . In fact, the temperature of any equilibrium stage can be determined in this way. We know that this is the temperature at which this vapour-liquid equilibrium occurs as each VLE is associated with exactly one temperature

We assume a particular column is isobaric because a unique Txy plot exists for each possible pressure. We can leverage this such that  $T_{min} \geq 30^\circ C$ . Simply increase the pressure to change  $T_{min}$ .

Figure 2.15: Txy at 1 atm

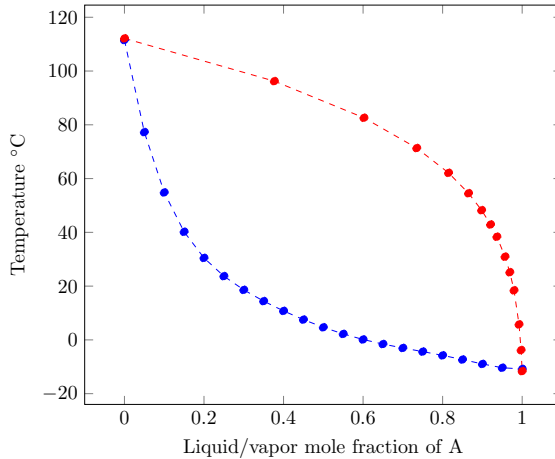
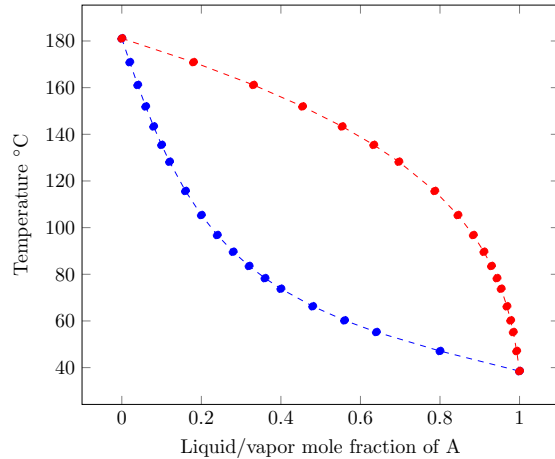


Figure 2.16: Txy at 5 atm



Notice how changing nothing but the pressure changes not just the location, but the shape of these curves. As a general trend, increasing pressure will increase  $T_{min}$ , after all

$$PV = nRT$$

Atmospheric pressure is still the cheapest option if possible, but it is by far cheaper to change the pressure than choose a different coolant.

## Column Efficiency

Up until this point, we have been assuming that our columns are operating with 100% efficiency. Clearly, neither you nor I are engineers talented enough to confidently assume this. To determine how we might calculate efficiency in this context, first we must consider what efficiency means for a given column or tray.

We have assumed that each tray achieves ideal vapour liquid equilibrium. This is the source of the inefficiency: distance from equilibrium. The answer to “How far from ideal VLE is this column?” is the efficiency of the column.

**Definition.** *The efficiency of a column or tray is its performance with respect to equilibrium*

How might efficiency be affected by the properties of the column? Efficiency is decreased by anything which might prohibit ideal vapour-liquid equilibrium behavior.

- Increased Viscosity
- Decreased Flowrates
- Decreased Mass Transfer Rates
- Poor Ease of Separation
- Small Column Size

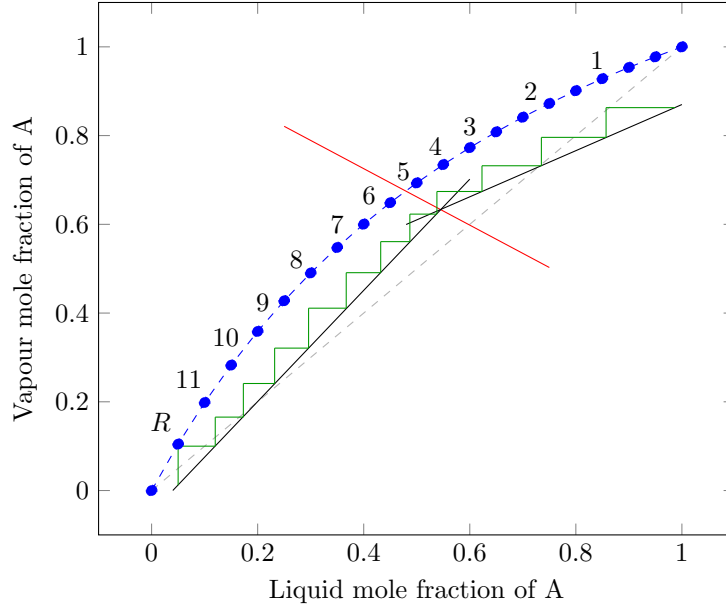
A particular method of measuring efficiency for a single tray, Murphree Efficiency, is represented with either a liquid or vapour basis, represented by  $E_{ML}$  and  $E_{MV}$  respectively. These two efficiencies are defined as the following

$$E_{MV} = \frac{y_j - y_{j+1}}{y^* - y_{j+1}} \quad (2.20)$$

$$E_{ML} = \frac{x_j - x_{j-1}}{x^* - x_{j-1}} \quad (2.21)$$

where the numerator represents the actual change in concentration and the denominator represents the change in concentration for an equilibrium stage. From this information we can determine the number of stages required for any given Murphree efficiency.

Figure 2.17: McCabe-Thiele Analysis for  $E_{MV} = 0.5$

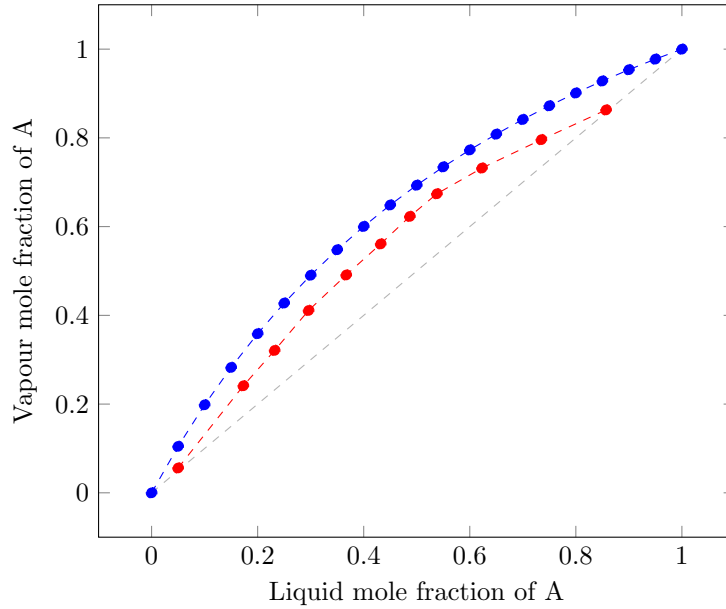


Note how each McCabe-Thiele stair only rises half of the way to the equilibrium line. The proportion it travels toward the equilibrium line is the ratio represented by  $E_{MV}$ . If the efficiency were to have been a Murphree liquid efficiency, then all of the horizontal lines would have been shortened, rather than the vertical.

To draw Murphree vapour efficiency, begin at  $(x_B, x_B)$  and continue your analysis until you reach  $(x_D, x_D)$ . Conversely, to draw Murphree liquid efficiency, begin at  $(x_B, x_B)$ , and travel down the graph. Also note that the line beneath the reboiler is unaffected by the efficiency. Even with a defined Murphree efficiency, we still treat the reboiler as ideal due to its extreme environment.

In a way, we are drawing our McCabe-Thiele analysis to a different equilibrium line, one representing the inefficient non-ideal equilibrium present to the column. We call this the pseudo-equilibrium line.

Figure 2.18: Psuedo-equilibrium line  $E_{MV} = 0.5$



Now that we know the number of trays needed to run this distillation at  $E_{MV} = 0.5$ , we can calculate the *Overall Efficiency*,  $E_o$ . This is the following ratio, where  $N$  represents the number of trays.

$$E_o = \frac{N_{ideal}}{N_{actual}} < 1 \quad (2.22)$$

Looking at this equation and the pseudo-equilibrium line, it should make sense that it requires more trays to complete a less ideal distillation. For example, the above has an overall efficiency of 0.45 since the ideal distillation requires 5 trays, and the  $E_{MV} = 0.5$  case requires 11. Note that

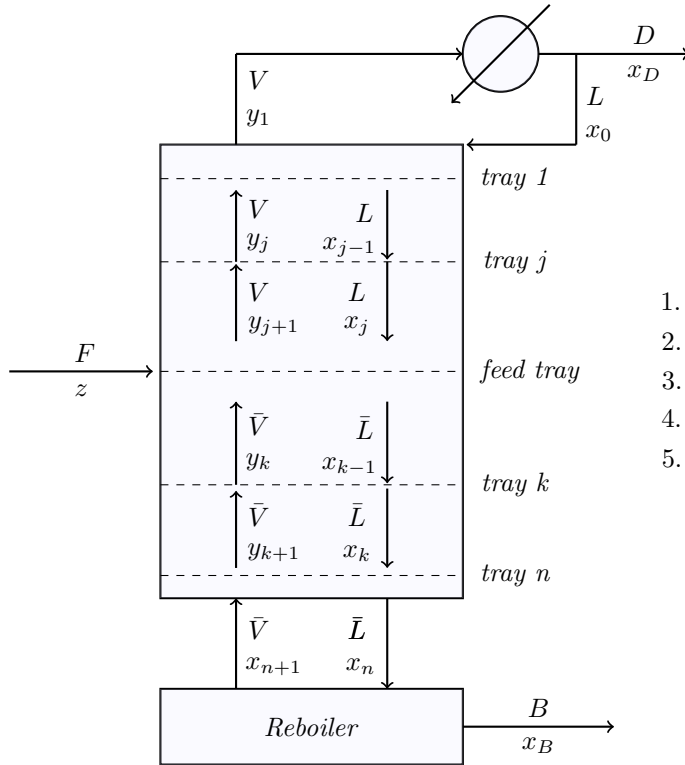
$$E_{MV} \neq E_{ML} \neq E_o$$

since all three of these measurements take different bases and measure efficiency differently.

## Chapter Review : Column Distillation

In this chapter, we learned about enriching and stripping columns, and total tray distillation. We learned to analyse separation processes via McCabe-Thiele analysis and defined the operating lines and feed line. Lastly, we learned to quantify efficiency, pressure, and temperature.

### Tray Distillation PFD



#### Assumptions:

1. Constant Molar Overflow (CMO)
2. Constant Pressure
3. Ideal Stages
4. Continuous Process at Steady State
5. No Reaction

#### Equations

1.  $y_k = \frac{\bar{L}}{\bar{V}}x_{k-1} - \frac{B}{\bar{V}}x_B$
2.  $y_k = \frac{R_B + 1}{R_B}x_{k-1} - \frac{1}{R_B}x_B$
3.  $y_j = \frac{L}{V}x_{j-1} + \frac{D}{V}x_D$
4.  $y_j = \frac{R}{1+R}x_{j-1} + \frac{1}{1+R}x_D$
5.  $Fz = Bx_B + Dx_D$
6.  $R_B = \frac{\bar{V}}{B}$
7.  $R = \frac{L}{D}$
8.  $q = \frac{\bar{L} - L}{F}$
9.  $1 - q = \frac{V - \bar{V}}{F}$
10.  $y = \frac{q}{q-1}x + \frac{z}{1-q}$
11.  $E_{MV} = \frac{y_j - y_{j+1}}{y^* - y_{j+1}}$
12.  $E_{ML} = \frac{x_j - x_{j-1}}{x^* - x_{j-1}}$
13.  $E_o = \frac{N_{ideal}}{N_{actual}} < 1$

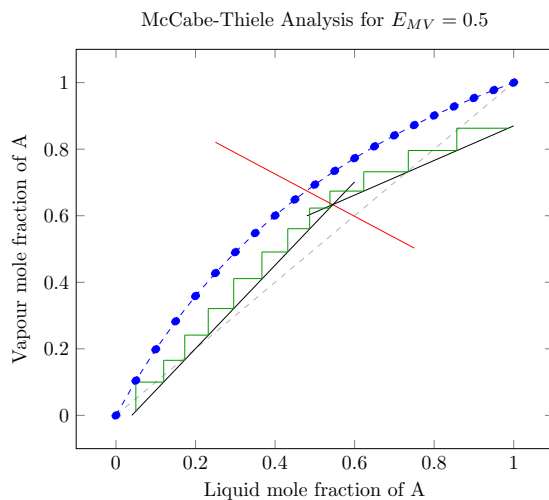
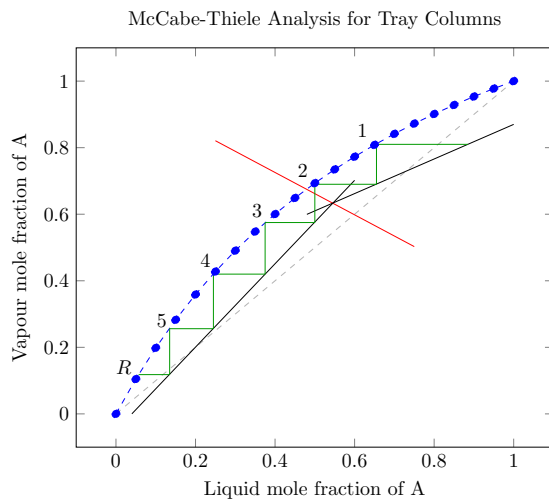
**1.** Stripping Operating Line **2.** Boilup Operating Line **3.** Enriching Operating Line **4.** Reflux Operating Line **5.** Partial Mass Balance **6.** Boilup Ratio **7.** Reflux Ratio **8-9.** Feed Quality **10.** Feed Line **11-12.** Murphree Efficiency **13.** Overall Efficiency

## Feed Line Information

Feed Type	$q$ -value	$q$ -line slope	$y$ -intercept
Subcooled Liquid	$q > 1$	positive	negative
Saturated Liquid	$q = 1$	$x = z$	N/A
Mixed Feed	$0 < q < 1$	negative	positive
Saturated Vapour	$q = 0$	$y = z$	$z$
Superheated Vapour	$q < 0$	positive	positive

## McCabe-Thiele Analysis

McCabe-Thiele Analysis can be drawn on  $x$ - $y$  plots to calculate the number of trays, tray composition, tray temperature and pressure, and optimal feed stage



## Inequalities

1.  $\frac{\bar{L}}{\bar{V}} \geq 1$
2.  $0 \leq \frac{L}{V} \leq 1$
3.  $T_{min} \geq 30^\circ C$
4.  $E_o < 1$

## Stripping Mass Balances

- $F = \bar{L}$
- $F = \bar{V} + B$
- $Fz = \bar{V}x + Bx_B$

## Enriching Mass Balances

- $F = L$
- $F = L + D$
- $Fz = Lx + Dx_D$

## Tray Distillation Balances

- $F = B + D$
- $Fz = Bx_B + Dx_D$
- $\bar{L} = \bar{V} + B$
- $V = L + D$

## Key Points

- Minimum trays occurs when operating lines are  $y = x$
- Maximum trays corresponds to minimum boilup and reflux
- $(x_B, x_B)$ ,  $(x_D, x_D)$ ,  $(z, z)$  lie on stripping, enriching, and feed lines respectively

**1.** Stripping Operating Line Slope **2.** Enriching Operating Line Slope **3.** Minimum Column Temperature **4.** Overall Efficiency



# Chapter 3

## Non-Discrete Equilibrium Stages

Until now, we have studied processes which have discrete trays which act as equilibrium stages. However, it is possible for there to be many more equilibrium environments, in which  $y$  gradually and continuously throughout the column.

### Gas Film Theory

The mechanism for gradient equilibrium change is different than the mechanism for discrete equilibrium stages. Recall that the driving force for tray distillation is vapour-liquid equilibrium. At each tray, vapour and liquid streams come equilibrium where the vapour stream is more pure with respect to the more volatile component. Clearly, vapour-liquid equilibrium between the two streams drives this process.

Gradient equilibrium change also exploits differences in volatility, but the driving force is no longer equilibrium itself.

#### Quick Facts.

- *Property Exploited: Volatility*
- *Driving Force: Mass Transfer*
- *Separation: Vapour/Liquid*

What is mass transfer? Consider a swimming pool with 5 kilolitres of water in the north half, and 1 kilolitre of water in the south half. What will happen? The net mass transfer will be southward, and very quickly, each half will contain 3 kilolitres of water. This is the principal that drives the gas film theory of mass transfer.

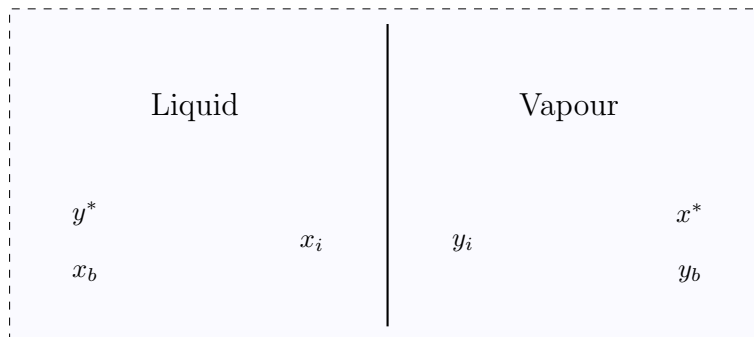


Figure 3.1 Gas Film Theory Model

There are three assumptions which are necessary to apply this model:

- No reactions
- Vapour and liquid exist on opposing sides of a laminar thin film interface
- Vapour liquid equilibrium exists at the interface

Within a process in which gas film theory applies, there are two key environments to study: the interface and the bulk. We assume that there exists a gas film membrane separating a large bulk of liquid from a large bulk of vapour. The liquid and vapour bulk compositions are represented by  $x_b$  and  $y_b$  respectively. Locally, near the membrane, is the interface. This is where liquid and vapour interact in equilibrium, denoted  $x_i$  and  $y_i$ . Since  $x_i$  and  $y_i$  are in equilibrium,  $x_i \neq x_b$  and  $y_i \neq y_b$ . Thus there is a concentration gradient between the bulk and the interface on either side of the gas film membrane.

This is our uneven swimming pool. If  $y_b > y_i$ , there will be a mass transfer from  $y_b$  to  $y_i$ . Although I liken this to water rushing to even out the water level of a swimming pool, a more accurate analogy would be dye placed in one corner of a pool, slowly diffusing until it evenly saturates the entire body of water. This drive towards diffusion, a concentration gradient, is the driving force of a gas film membrane.

If  $y_b > y_i$ , then there will be mass transfer towards  $y_i$ , thus  $y_i$  will increase. But,  $y_i$  is in equilibrium with  $x_i$ , so mass is transferred across the membrane, increasing  $x_i$ . Then, since  $x_i > x_b$ , mass is transferred from the liquid interface to the liquid bulk. By this mechanism, mass is transferred from the vapour bulk to the liquid bulk, and the flow of mass across the gas film membrane is called flux.

**Definition.** Flux is the rate of mass transfer across a membrane, per surface area of the membrane

In this way, flux can be quantified as proportional to the driving force, the concentration gradient represented by the difference between the bulk and the interface.

$$N_A = k_y(y_b - y_i) \tag{3.1}$$

$$N_A = k_y(y_i - y_b) \tag{3.2}$$

$$N_A = k_x(x_b - x_i) \tag{3.3}$$

$$N_A = k_x(x_i - x_b) \tag{3.4}$$

In order, these equations are:

- Flux from vapour bulk to vapour interface
- Flux from vapour interface to vapour bulk
- Flux from liquid bulk to liquid interface
- Flux from liquid interface to liquid bulk

Flux depends on two distinct factors. The component with respect flux is calculated, and the direction of the flux. There are two mass transfer coefficients that can be used here,  $k_y$  and  $k_x$ . These represent the factors other than the concentration gradient which affect flux. When calculating flux with respect to vapour concentrations, it is necessary to use  $k_y$ , and for flux calculations with respect to liquid concentrations,  $k_x$  must be used. The driving force used reflects the direction of mass transfer. For example, if  $(y_b - y_i)$  is used, the flux is reported in terms of transfer from the vapour bulk to the vapour interface. This calculation will be equal and opposite to the calculation from interface to bulk.

Flux represents mass transfer across an interface, and the units of flux reflect this. The units of flux are

$$\frac{\text{quantity}}{\text{area} \cdot \text{time}}$$

which, for a molar flow, may take the form of

$$\frac{\text{mol}}{\text{m}^2 \cdot \text{min}}$$

Importantly, the units of the mass transfer coefficient are the same as the units for flux, since the change in concentration is treated as a unitless quantity.

When calculating the flux as the mass transfer from the bulk to interface, we use  $k_x$  and  $k_y$ , which are referred to as the *individual phase* mass transfer coefficients. We can also consider the mass transfer from bulk to bulk, represented by the concentration gradient between  $x_b$  and  $x^*$  or  $y_b$  and  $y^*$ . In this example  $x^*$  and  $y^*$  are in equilibrium with the vapour and liquid bulk respectively. For this calculation, the *overall phase* mass transfer coefficients  $K_x$  and  $K_y$  are used. Calculating flux using overall mass transfer coefficients would take the form:

$$N_A = K_x(x^* - x_b) \tag{3.5}$$

$$N_A = K_y(y^* - y_b) \tag{3.6}$$

## Packed Columns

Although gas film theory can be applied to generic mass transfer scenarios, it is particularly useful in the analysis of packed columns, a near cousin of the distillation column. A packed column is a distillation column which, rather than contain discrete trays, contains *packing*, pieces of specialised material which provides the vapour-liquid interface. As such, the analysis techniques used for tray distillation cannot be applied since there are no equilibrium stages.

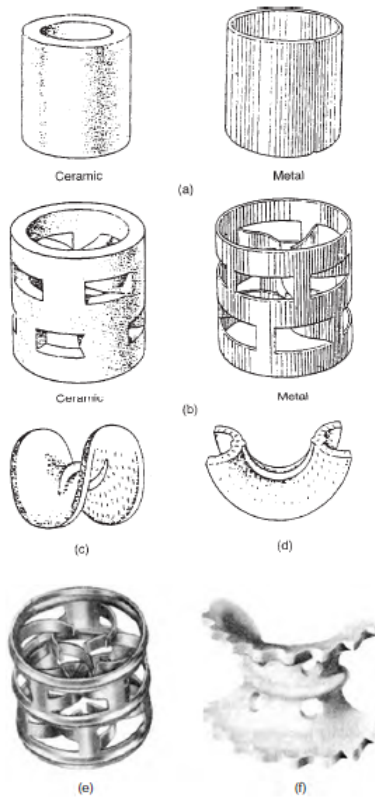


Figure 3.2 Types of Packing

Depending on the separation, different packing materials and shapes are used. Particularly, it is imperative that the packing material does not react with either component of the separation. It is on the surface area of the packing where the interface between the vapour and liquid bulk occurs. Generally, it is necessary to use packing which is lightweight, offers satisfactory amounts of interface area, usually denoted as  $a$ , facilitates vapour and liquid flow without holdup or pressure drop, and is cost-effective.

**Quick Facts.**

- *Property Exploited: Volatility*
- *Driving Force: Mass Transfer*
- *Separation: Vapour/Liquid*

Below is a PFD of a packed column:

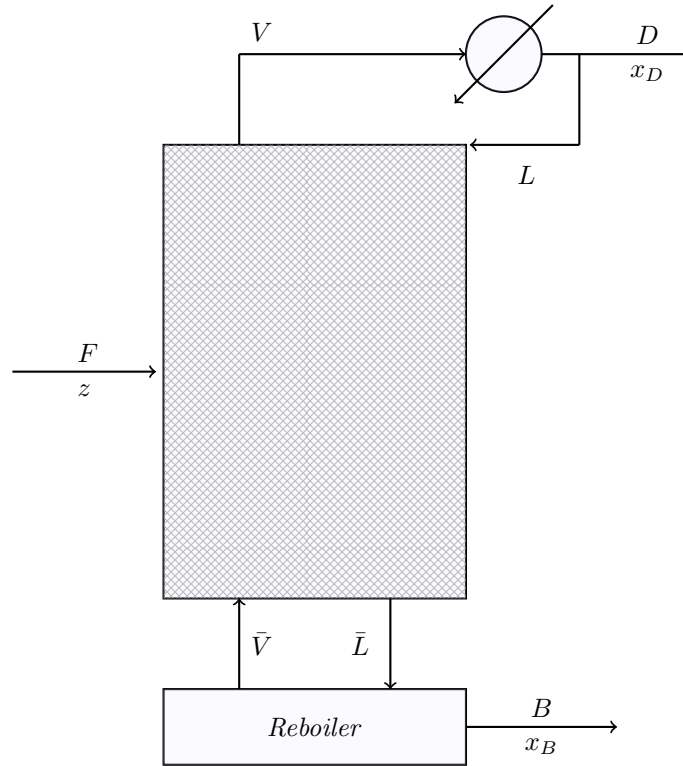


Figure 3.3: PFD of Packed Column

Structurally a packed column is very similar to a tray column, the only difference being the internals. The assumptions are also analogous:

1. Equimolar Counterdiffusion
2. Constant Pressure
3. Continuous Process at Steady State
4. No Reaction

What is equimolar counterdiffusion? This is the packed column equivalent to CMO, the assumption which enables us to treat all liquid and vapour flowrates within a section of the column as equal. Equimolar counterdiffusion supposes that diffusion across the interface does not result in a net change of mass. For every mole of component  $A$  that crosses the interface, a mole of  $B$  crosses the interface in the opposite direction. This way the concentration of both bulk systems varies without changing the net flowrate of the stream.

## Transfer Unit Analysis

Since there are no stages, it should come as no shock that McCabe-Thiele analysis cannot be used to analyse a packed column. Instead, we need to consider the mass transfer which occurs in a differential height of the column. Rather than find the number of trays necessary, we will calculate the total height needed to achieve our desired distillation. By using calculus, we can turn an equilibrium gradient into an infinite sum of infinitesimal stages. One of these differential heights is labeled on the diagram below.

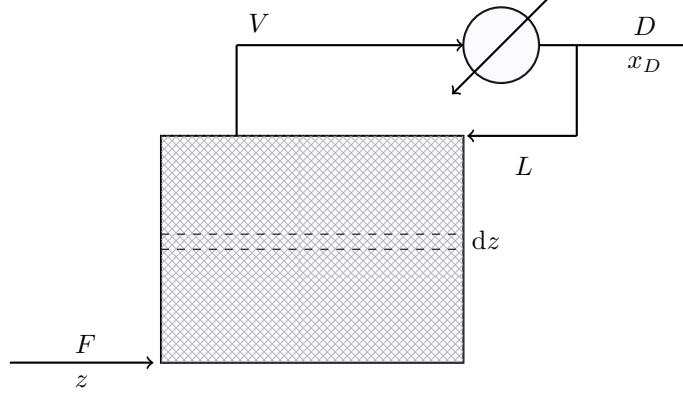


Figure 3.4: Differential Height of Packed Column

If we can calculate the flux inside this differential volume of the column, we can integrate to find the total mass transfer of the column. The resulting equation is a restating of 3.1, derived in Appendix A.

$$N_A a A_c dz = k_y (y_i - y) a A_c dz \quad (3.7)$$

The term  $A_c$  represents the cross sectional area of the column, thus  $a A_c dz$  is the differential volume of the column multiplied by the interface surface area. Both sides of this equation calculate the flux, the amount of component  $A$  transferred between phases (in this case from liquid to vapour) per area of interface, multiplied by the interface area available per volume, multiplied by the volume. Simplifying away these rates, we are left with the amount of  $A$  transferred per time! The net transfer of  $A$  from liquid to vapour can be represented as  $L dx_A$  or  $V dy_A$ , the flowrate multiplied by the change in concentration

$$N_A a A_c dz = L dx_A = V dy_A \quad (3.8)$$

$$k_y (y_i - y) a A_c dz = L dx_A = V dy_A \quad (3.9)$$

Solving this equation for the height of the column, we get

$$h_e = \frac{V}{k_y a A_c} \int_{y_{in,e}}^{y_{out,e}} \frac{dy_A}{(y_i - y)} \quad (3.10)$$

$$h_e = \frac{L}{k_x a A_c} \int_{x_{out,e}}^{x_{in,e}} \frac{dx_A}{(x - x_i)} \quad (3.11)$$

So far, we have been solving in terms of an enriching column. For those with a greater affinity for stripping, these equations can be modified to solve for a stripping column. Just as McCabe-Thiele analysis requires two operating lines to solve a total tray column, to perform transfer unit analysis on a packed column with both a stripping and enriching section, the height of each must be calculated independently.

$$h_s = \frac{\bar{V}}{k_y a A_c} \int_{y_{in,e}}^{y_{out,e}} \frac{dy_A}{(y_i - y)} \quad (3.12)$$

$$h_s = \frac{\bar{L}}{k_x a A_c} \int_{x_{out,e}}^{x_{in,e}} \frac{dx_A}{(x - x_i)} \quad (3.13)$$

These equations can also be solved in terms of bulk-to-bulk overall mass transfer. Recall that  $x^*$  is the liquid in equilibrium with  $y_b$ , and  $y^*$  is the vapour in equilibrium with  $x_b$

$$h_e = \frac{V}{K_y a A_c} \int_{y_{in,e}}^{y_{out,e}} \frac{dy_A}{|y^* - y|} \quad (3.14)$$

$$h_e = \frac{L}{K_x a A_c} \int_{x_{out,e}}^{x_{in,e}} \frac{dx_A}{|x - x^*|} \quad (3.15)$$

$$h_s = \frac{\bar{V}}{K_y a A_c} \int_{y_{in,e}}^{y_{out,e}} \frac{dy_A}{|y^* - y|} \quad (3.16)$$

$$h_s = \frac{\bar{L}}{K_x a A_c} \int_{x_{out,e}}^{x_{in,e}} \frac{dx_A}{|x - x^*|} \quad (3.17)$$

In actual applications, this is the calculation that is almost always being performed. To calculate with respect to the individual phase transfer would require a measurement of the composition at the interface, something quite difficult to perform on an operating column. Whereas, overall phase transfer only requires equilibrium information and an operating line, where  $x$  and  $y$  are points on the operating line and  $x^*$  and  $y^*$  are points on the equilibrium curve.

This quantity that is being integrated is the inverse of the driving force, the concentration gradient of the components. As such, it is called the *resistance*. As this is almost never an analytic function, to calculate the integral of the resistance, it is necessary to graph the resistance versus the change in concentration, and take a rough integral by estimating the area under the curve.

## HTUs and NTUs

You may have noticed that all of these equations have a very similar form, that the height is the product of some constant and an integral. The left part of the product is the *height of the transfer unit* whereas the right part of the product is the *number of transfer units*. These are the imaginary, differential, trays which a packed column contains. For example, the height of an enriching column can be expressed as the following.

$$h_e = (HTU)_{OL} (NTU)_{OL}$$

This is equivalent to Equation 3. Here, the subscript *OL* represents that this is the overall calculation, bulk-to-bulk, and done with a liquid basis. The same calculation could be performed with respect to a vapour basis, or the individual mass transfer. Importantly, however, you cannot mix and match within a single equation. If you calculate  $(HTU)_{IG}$ , you must also use  $(NTU)_{IG}$ . Crucially, the resulting height from any method of calculation should be equivalent.

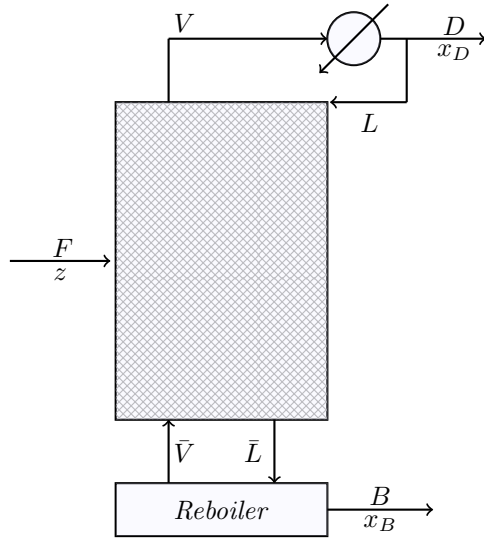
We can further relate packed columns to tray columns by calculating the *Height Equivalent of a Theoretical Plate* or *HEPT*, which is the height of packing of a packed column which corresponds to one equilibrium stage on a tray column. HEPT can be calculated by the following.

$$HEPT = \frac{\text{total height of packing}}{\text{number of theoretical stages}} \quad (3.18)$$

## Chapter Review : Non-Discrete Equilibrium Stages

In this chapter, we learned about packed columns, a unit operation without discrete equilibrium stages. As such, novel analysis methods must be applied, mainly transfer unit analysis, which is derived from gas-film theory.

### Packed Column PFD



### Packed Column Assumptions

1. No Reactions
2. Steady-State and Continuous
3. Constant Pressure
4. Equimolar Counterdiffusion

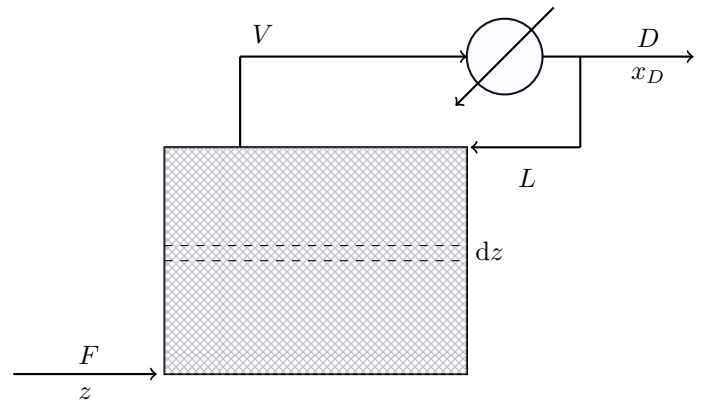
### Equations

1.  $N_A = k_y(y_b - y_i)$
2.  $h_e = \frac{V}{K_y a A_c} \int_{y_{in,e}}^{y_{out,e}} \frac{dy_A}{|y^* - y|}$
3.  $h_e = \frac{L}{K_x a A_c} \int_{x_{out,e}}^{x_{in,e}} \frac{dx_A}{|x - x^*|}$
4.  $h_s = \frac{\bar{V}}{K_y a A_c} \int_{y_{in,e}}^{y_{out,e}} \frac{dy_A}{|y^* - y|}$
5.  $h_s = \frac{\bar{L}}{K_x a A_c} \int_{x_{out,e}}^{x_{in,e}} \frac{dx_A}{|x - x^*|}$
6.  $h_e = (HTU)_{OL} (NTU)_{OL}$
7.  $HEPT = \frac{\text{total height of packing}}{\text{number of theoretical stages}}$

1. Example of Flux **2-5**. Overall height calculations **6**. HTU/NTU form **7**. HEPT

### Differential Height of a Column

To perform transfer unit analysis, we must integrate the concentrations of the more volatile component at different differential heights of the column.



### Properties

- Property Exploited: Volatility
- Driving Force: Mass Transfer
- Separation: Vapour/Liquid

### Key Points

- Flux can be calculated in any area and the direction must be defined.
- The units of flux are quantity per area times time
- $x^*$  and  $y^*$  is in equilibrium with the bulk
- Packing is chosen to be cost-efficient and non-reactive
- When calculating column height, do not mix overall with individual, nor liquid basis with vapour basis



# Extraction and Absorption

Although we have spent our time up until now analysing distillation, there are many more types of separation processes, all of which are guided by the same general principles. We will take this time now to understand two new processes, extraction and absorption, with the goal of laying the groundwork for understanding any and all separation processes.

## Liquid-Liquid Extraction

Liquid-Liquid Extraction is a separation process wherein a solute is dissolved out of a feed stream via a solvent. While still a process dependant on equilibrium, the equilibrium present is solubility-based equilibrium, rather than VLE. Similar to tray columns, extraction units have discrete trays with discrete equilibrium stages.

### Quick Facts.

- *Property Exploited: Solubility*
- *Driving Force: Solubility-Based Equilibrium*
- *Separation: Liquid/Liquid*

The feed, referred to as the *diluent* or *raffinate*, contains some dissolved component called the *solute*. Within the unit, the diluent comes in contact with the *solvent*, or *extract* stream. Since the solvent is chosen such that the solute is more soluble in the solvent than in the diluent, the solute is transferred from the diluent to the solvent. The result of this process is that the diluent is purified of the solute. It may be helpful to see this in terms of a PFD

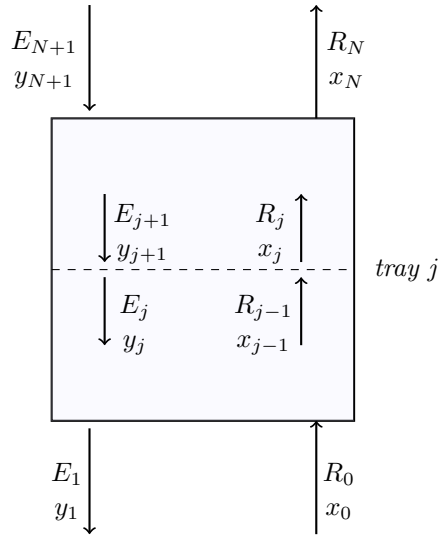


Figure 4.1 PFD of Liquid-Liquid Extraction

It is important to note that although the extract and raffinate streams are both liquids, they are treated as two distinct phases for analysis. For this context, we denote the composition of the solute in the raffinate as  $x$  and the composition of the solute in the extract as  $y$ . Note also that the raffinate and extract streams oppose each other. This is called a *counter-current system*. Although it is possible and sometimes necessary to construct a *co-current system*, where both raffinate and extract streams enter the and leave the same side of the unit, this is far less efficient.

The assumptions for an extraction unit are as follows:

- Isothermal and Isobaric
- No Reaction
- Heat of Mixing is Negligible
- Diluent and Solvent are Totally Immiscible
- System is Dilute

Note that if the system were not dilute, the transfer of the solute from diluent to solvent would change the flowrates. Also note that if the diluent and solvent could mix, the system would not be able to separate anything. Just as in distillation, it is necessary to assume that the flowrates of the raffinate and extract from each tray are equal. That is to say  $R$  and  $E$  are constant.

Drawing a mass balance around any tray  $j$  and the top of the column, the following operating can be derived. This derivation will be left as an exercise to the reader.

$$y = \frac{R}{E}x + \left( y_{n+1} - \frac{R}{E}x_N \right) \quad (4.1)$$

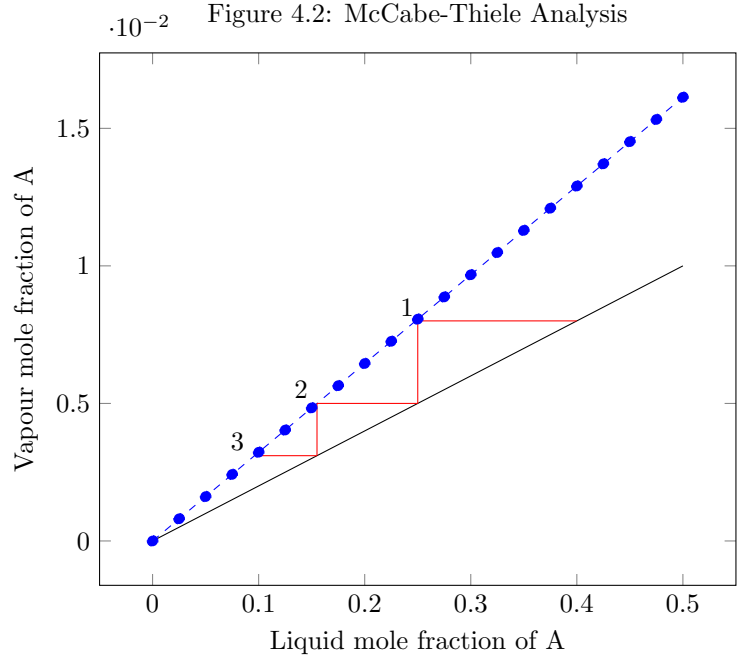
Given the standard interpretation of an operating line as the points leaving or entering one side of a tray, it should follow that the points  $(x_0, y_1)$  and  $(x_N, y_{N+1})$  will always fall on the operating line. The former represents the point of least concentration in both streams, and the latter represents the point of most concentration in both streams. Note that the  $y$  values would be swapped between the points if this were a co-current system.

# McCabe-Thiele Analysis: Extraction

McCabe-Thiele Analysis for an extraction unit is quite similar to all previous McCabe-Thiele procedures. Unlike in vapour-liquid systems, equilibrium information for solubility-based systems is often linear and given by the *distribution ratio*  $K_d$ , which is defined as

$$K_d = \frac{y_A}{x_A} \tag{4.2}$$

The following is an example McCabe-Thiele plot for an extraction system, where  $K_d = 1/31$



Notice how stage 1, the bottom of the unit, is where the compositions are the greatest. This should make sense with our understanding of a counter-current extraction operation. The  $y$ -axis scale here is minuscule. Since the driving force is solubility based equilibrium, it is necessary for the difference in concentration between the raffinate and extract streams to be large. Similar to how a packed column will not distil if the concentration gradient is small, an extraction unit is rather useless without a near-pure solvent.

## Absorption

Absorption is a separation process quite similar to extraction, however with one key difference: the phase of the feed. In an absorption system, a vapour *carrier gas* is purified of the solute by being passed through a liquid solvent. The solute dissolves out of the gas and into the solvent. Just like extraction this is an equilibrium stage process with discrete stages.

### Quick Facts.

- *Property Exploited: Solubility*
- *Driving Force: Solubility-Based Equilibrium*
- *Separation: Liquid/Liquid*

As both extraction and absorption operate quite similarly, the PFDs for both operations are analogous.

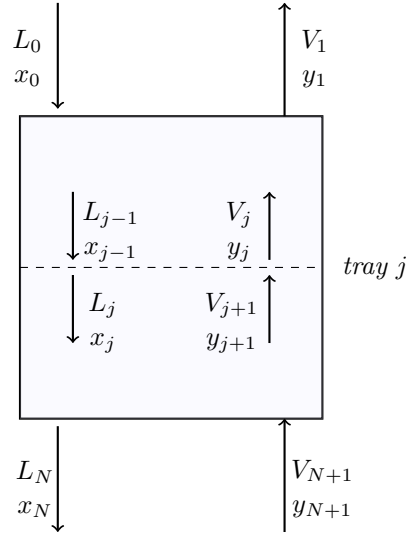


Figure 4.3 PFD of Total Flowrate Absorption

Importantly, *tray N* is now the tray at the bottom of the unit, rather than at the top as in extraction. Co-current absorption systems do exist, however, due to inefficiency, they are rarely considered.

The assumptions for an extraction unit are as follows:

- Isothermal and Isobaric
- No Reaction
- Steady State and Continuous
- Carrier Gas is Insoluble
- Solvent is Nonvolatile
- System is Dilute

These last three assumptions enable us to assume that the liquid and gas flow throughout the unit are constant. If the carrier gas could dissolve in the solvent, the operation would essentially break, and if the solvent was volatile, some of it would vaporize into the carrier gas.

By drawing a mass balance around a single tray and the top of the column, we can derive the operating line, which, once again, will be left as an exercise to the reader.

$$y = \frac{L}{V}x + \left( y_1 - \frac{L}{V}x_0 \right) \quad (4.3)$$

## Carrier Basis

Can we always consider the system to be dilute? The carrier gas has the potential to be saturated with a significant amount of solute. In this case, we can no longer ignore the mass transfer of solute

from the carrier gas to the extract stream. For the threshold between a dilute and non-dilute system, we have the following heuristic

$$y_0 \leq 0.05$$

That the feed is less than or equal to 5% solute. If this is not the case, we need to develop a new basis for understanding our process.

Non-dilute systems are near impossible to analyse via the total flowrate basis which we have been using thus far because the total flowrate from each tray is no longer constant. This results in a piecewise linear operating line, which is not useful for McCabe-Thiele analysis. We can, however, solve this problem by understanding what is constant in this system.

The flowrate of the carrier gas itself, agnostic to the solute diluted within, does not change throughout the process. Neither does the flowrate of the solvent, if we ignore the solute which it dissolves. This understanding of a process is called the *carrier flowrate basis*, and will enable us to wield the power of McCabe-Thiele analysis for non-dilute systems.

The PFD of an Absorption unit can be expressed via the carrier flowrate basis.

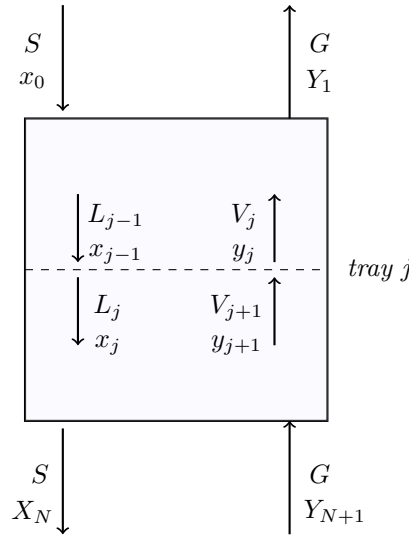


Figure 4.4 PFD of Carrier Flowrate Absorption

Here,  $G$  represents the flowrate of the carrier gas, and  $S$  represents the flowrate of the solvent. We can define  $F_{solute}$  to be the flowrate of the solute. While  $G$  and  $S$  are constant throughout the trays,  $F_{solute}$  varies from tray to tray.

What are  $X$  and  $Y$ ? First, it is important to understand exactly what  $x$  signifies. If a stream has composition  $x = 0.2$ , that means that 20% of the total liquid stream is comprised of the component in question. We call this the component fraction, and importantly, it is taken with respect to the total stream. Now consider  $X$ , the *component ratio*.

**Definition.** *The component ratio is the ratio of the amount of component in the stream and the amount of pure carrier or solvent in the stream*

We can calculate  $X$  and  $Y$  by the following

$$X = \frac{x}{1 - x} \tag{4.4}$$

$$Y = \frac{y}{1 - y} \tag{4.5}$$

This relationship is true because if  $x$  represents the fraction of solute  $1 - x$  represents the fraction of solvent, both when compared to the total stream.

Using this PFD and the component ratios, we can derive an operating line similar to that for a dilute system. This operating will be linear for a non-dilute system, making McCabe-Thiele analysis possible.

$$Y = \frac{S}{G}X + \left( Y_1 - \frac{S}{G}X_0 \right) \quad (4.6)$$

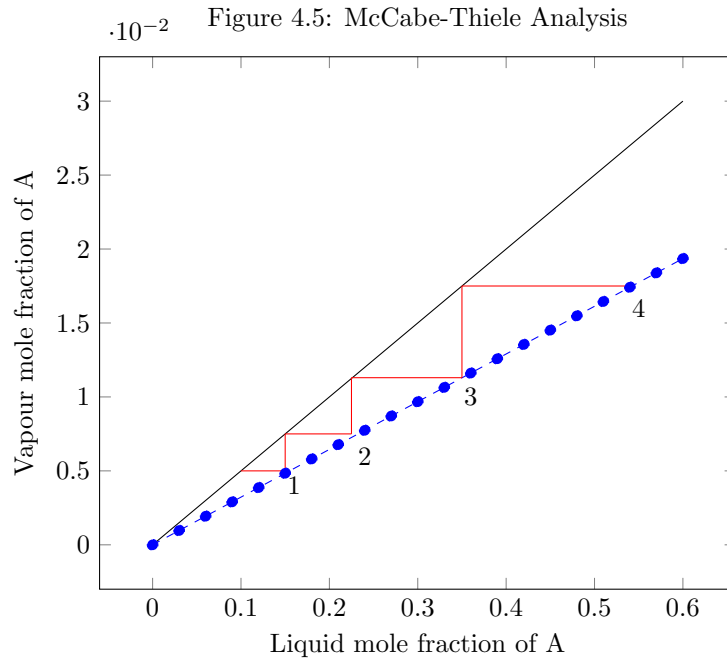
## McCabe-Thiele Analysis: Absorption

Equilibrium information for an absorption system is frequently derived from Henry's law

$$y = \frac{H}{P_{total}}x \quad (4.7)$$

where  $y$  and  $x$  are the component fraction of the solute in vapour and liquid phase respectively,  $P_{total}$  is the total pressure of the system, and  $H$  is the *Henry's Law Constant* for the system. Raoult's Law 1.5 can also be used as a thermodynamic model for equilibrium in absorption. For dilute systems, it is preferred to use Henry's Law, and for concentrated systems, it is more accurate to use Raoult's Law.

McCabe-Thiele analysis itself will look slightly different for absorption, although the methodology is the same, because in this case, the component in question is flowing from vapour to liquid, as opposed to in distillation, where the more volatile component flows from liquid to vapour.



The operating line is now above the equilibrium line, and the entire process is done the same as before, but now reflected over the equilibrium line. Also note that the largest concentration is represented by the largest stage, and the stages are numbered from left to right, as opposed to from right to left. In order to use the information gained by McCabe-Thiele analysis here, it becomes necessary to convert back from a carrier basis for a concentrated system.

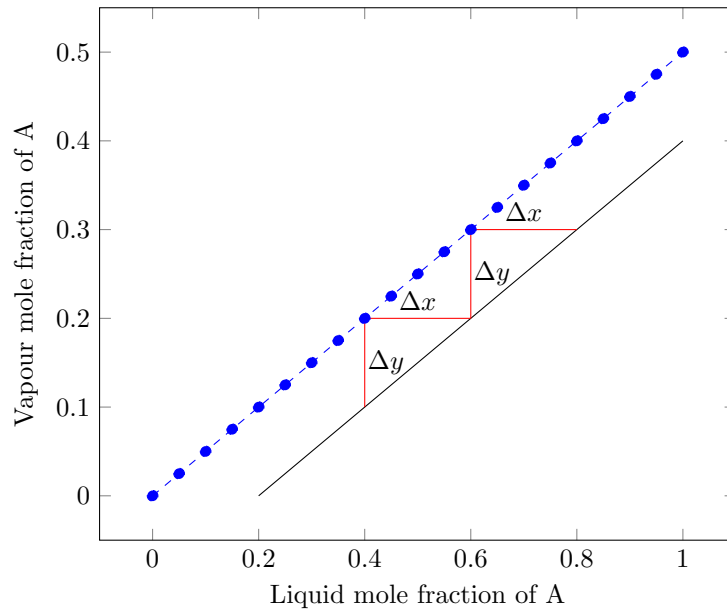
# Kresmer Equations

We have spent a significant amount of time deriving and performing McCabe-Thiele analysis. It is only fitting that we end with an alternative. McCabe-Thiele analysis can be tedious, time consuming, and inefficient, all of which can be avoided with the Kresmer Equations.

To begin, for dilute systems, consider the case of linear equilibrium, where the equilibrium line is a linear equation. If this is true, an important observation can be made about the relationship between the different McCabe-Thiele *stairs* one must draw to calculate the ideal number of stages.

This relationship is best observed when the operating line is parallel to the equilibrium line

Figure 4.6: Parallel Lines



Notice how  $\Delta x$  and  $\Delta y$  are constant? For any linear operating and equilibrium lines, we can relate the length and height of each stair to calculate the number of ideal stages algebraically. This statement can be expressed as the equation

$$(y_1 - y_{N+1}) = (\Delta y) \cdot N$$

where  $(y_1 - y_{N+1})$  is the total change in  $y$  throughout the process. The same relationship holds for the change in  $x$ . Although this relationship is only true when the lines are parallel, i.e.  $\Delta y$  is constant, an analogous relationship can be defined for all linear operating and equilibrium lines.

First we define the *extraction factor* to be

$$\frac{R}{mE}$$

where  $m$  is the slope of the equilibrium line. If

$$\frac{R}{mE} = 1$$

we know that these two lines are parallel. We can also define an *absorption factor* for dilute absorptions

$$\frac{L}{mV}$$

From these relationships the Kresmer equations can be derived. In the case of parallel lines we get

$$N = \frac{y_{N+1} - y_1}{y_1 - (R/E)x_0 - b} \quad (4.8)$$

$$N = \frac{y_{N+1} - y_1}{y_1 - (L/V)x_0 - b} \quad (4.9)$$

Where  $b$  is the  $y$ -intercept of the operating line. In the case of non-parallel lines we get

$$N = \frac{\ln \left[ \left( 1 - \frac{mE}{R} \right) \left( \frac{y_{N+1} - y_1^*}{y_1 - y_1^*} \right) + \left( \frac{mE}{R} \right) \right]}{\ln \left[ \frac{R}{mE} \right]} \quad (4.10)$$

$$N = \frac{\ln \left[ \left( 1 - \frac{mV}{L} \right) \left( \frac{y_{N+1} - y_1^*}{y_1 - y_1^*} \right) + \left( \frac{mV}{L} \right) \right]}{\ln \left[ \frac{L}{mV} \right]} \quad (4.11)$$

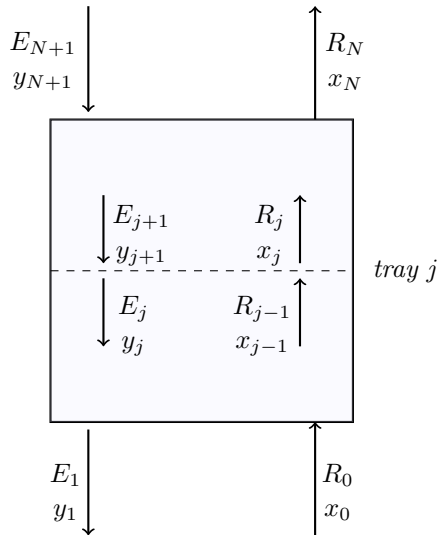
With these equations we are able to calculate the number of ideal stages algebraically so long as the equilibrium line is linear and the system is dilute.



## Chapter Review : Extraction and Absorption

In this chapter, we introduced two new separation processes, Extraction and Absorption, which operate from a new type of equilibrium, solubility. We then learned how to analyse a non-dilute system, finally discovering an algebraic way to calculate the number of ideal stages via the Kresmer equations.

### Extraction PFD



### Equations

1.  $y = \frac{R}{E}x + \left(y_{n+1} - \frac{R}{E}x_N\right)$
2.  $K_d = \frac{y_A}{x_A}$
3.  $y = \frac{L}{V}x + \left(y_1 - \frac{L}{V}x_0\right)$
4.  $y_0 \leq 0.05$
5.  $X = \frac{x}{1-x}$
6.  $Y = \frac{y}{1-y}$
7.  $Y = \frac{S}{G}X + \left(Y_1 - \frac{S}{G}X_0\right)$
8.  $y = \frac{H}{P_{total}}x$

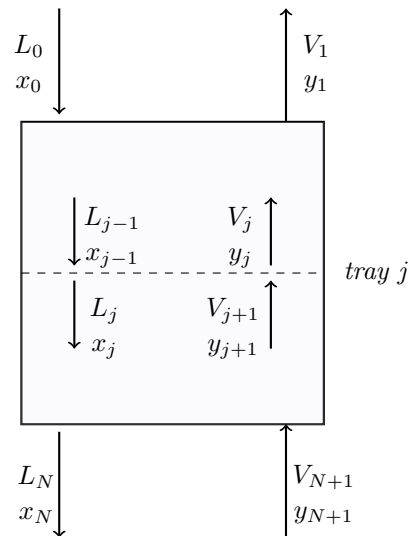
### Extraction Assumptions

1. Isothermal and Isobaric
2. No Reaction
3. Heat of Mixing is Negligible
4. Diluent and Solvent are Totally Immiscible
5. System is Dilute

### Key Points

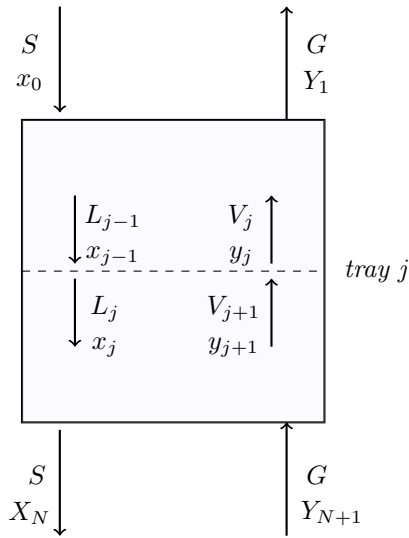
- The Kresmer Equations can be used when equilibrium is linear and the system is dilute
- Carrier flowrate basis is used when system is concentrated
- The liquid raffinate and extract streams are distinct phases in extraction

### Absorption Total Flowrate Basis PFD

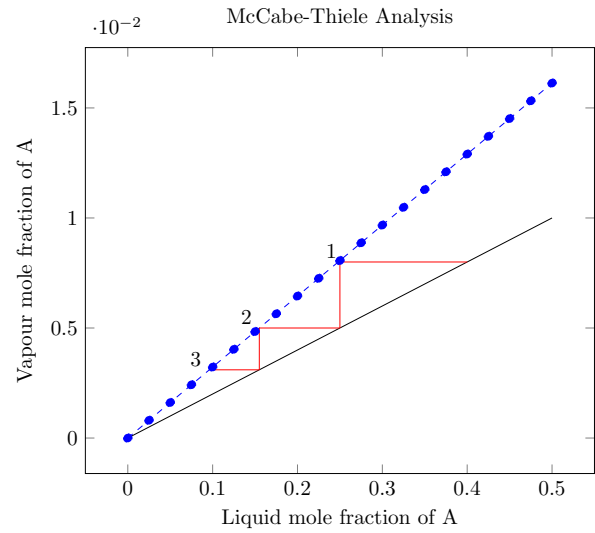


**1.** Extraction Operating line **2.** Distribution Ratio **3.** Absorption Operating Line **4.** Concentrated System Threshold **5-6.** Component Ratio **7.** Absorption Carrier Operating Line **8.** Henry's Law

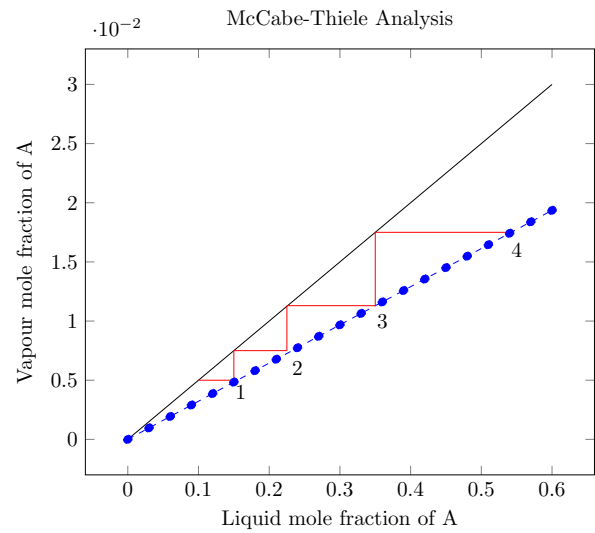
## Absorption Carrier Basis PFD



## McCabe-Thiele Extraction



## McCabe-Thiele Absorption



## Properties

- Property Exploited: Solubility
- Driving Force: Solubility-Based Equilibrium
- Absorption Separation: Gas-Liquid
- Enriching Separation: Liquid-Liquid

## Kresmer Equations

- $$N = \frac{y_{N+1} - y_1}{y_1 - (R/E)x_0 - b}$$
- $$N = \frac{y_{N+1} - y_1}{y_1 - (L/V)x_0 - b}$$
- $$N = \frac{\ln \left[ \left( 1 - \frac{mE}{R} \right) \left( \frac{y_{N+1} - y_1^*}{y_1 - y_1^*} \right) + \left( \frac{mE}{R} \right) \right]}{\ln \left[ \frac{R}{mE} \right]}$$
- $$N = \frac{\ln \left[ \left( 1 - \frac{mV}{L} \right) \left( \frac{y_{N+1} - y_1^*}{y_1 - y_1^*} \right) + \left( \frac{mV}{L} \right) \right]}{\ln \left[ \frac{L}{mV} \right]}$$

# Conclusion

I have given my best attempt at explaining every concept, every lesson, every equation, and every graph contained within CHEG 302, Separation Processes. This project has been the product of hours, so many long days and long nights. This might be the longest document I have ever produced. Of this I am proud.

I hope this has been useful, I hope this has been well. I hope my meticulous diagrams are captivating, I hope my painfully typeset equations are beautiful. I hope this is what I wanted it to be. Du Bellay returned from Rome, returning to his paradise angevine. And now, I have completed CHEG 302.

I write this for my Muse. Not that they would bother to tolerate all these pages, nor that they would care for flowrates and carrier bases, but that they know I did it. That I *could* do it. With that passion, this I have written, this I have finished, this I have loved.

~ Sofi

# Appendix A: Proofs and Derivations

## A.1. Boilup Stripping Operating Line

This is a proof of Equation 2.5. Given the following,

$$R_B = \frac{\bar{V}}{B} \quad (\text{A.1})$$

$$y_k = \frac{\bar{L}}{\bar{V}}x_{k-1} - \frac{B}{\bar{V}}x_B \quad (\text{A.2})$$

$$\bar{L} = \bar{V} + B \quad (\text{A.3})$$

We can substitute A.3 into A.2

$$y_k = \frac{\bar{V} + B}{\bar{V}}x_{k-1} - \frac{B}{\bar{V}}x_B$$

Then, the right side of the equation can be multiplied by

$$\frac{1/B}{1/B}$$

Which yields

$$y_k = \frac{\bar{V}/B + 1}{\bar{V}/B}x_{k-1} - \frac{1}{\bar{V}/B}x_B$$

Substituting for A.1, we get

$$y_k = \frac{R_B + 1}{R_B}x_{k-1} - \frac{1}{R_B}x_B \quad (\text{2.5})$$

□

## A.2. Reflux Enriching Operating Line

This is a proof of Equation 2.10. Given the following

$$R = \frac{L}{D} \quad (\text{A.4})$$

$$y_j = \frac{L}{V}x_{j-1} + \frac{D}{V}x_D \quad (\text{A.5})$$

$$V = L + D \quad (\text{A.6})$$

We can substitute A.6 into A.5

$$y_j = \frac{L}{L + D}x_{j-1} + \frac{D}{L + D}x_D$$

Then, the right side of the equation can be multiplied by

$$\frac{1/D}{1/D}$$

Which yields

$$y_j = \frac{L/D}{L/D + 1} x_{j-1} + \frac{D}{L/D + D} x_D$$

Substituting for A.4, we get

$$y_j = \frac{R}{R+1} x_{j-1} + \frac{1}{R+1} x_D \quad (2.10)$$

□

### A.3. Derivation of the q-line

This is a proof of Equation 2.19. Given the following mass balances for a tray column

$$\bar{V}y + \bar{L}x - Bx_B \quad (A.7)$$

$$Vy = Lx + Dx_D \quad (A.8)$$

We can subtract A.8 from A.7 to get

$$\bar{V}y - Vy = \bar{L}x - Lx - Bx_B - Dx_D$$

And can be rearranged as

$$y(\bar{V} - V) = (\bar{L} - L)x - (Bx_B + Dx_D)$$

Dividing both sides by  $\bar{V} - V$ , we get

$$y = \frac{\bar{L} - L}{\bar{V} - V} x - \frac{Bx_B + Dx_D}{\bar{V} - V}$$

Then we can multiply the right side by  $F/F$

$$y = \left( \frac{F}{F} \cdot \frac{\bar{L} - L}{\bar{V} - V} \right) x - \left( \frac{F}{F} \cdot \frac{Bx_B + Dx_D}{\bar{V} - V} \right)$$

Which can be rearranged as

$$y = \left( \frac{\bar{L} - L}{F} \cdot \frac{F}{\bar{V} - V} \right) x - \left( \frac{F}{\bar{V} - V} \cdot \frac{Bx_B + Dx_D}{F} \right) \quad (A.9)$$

We can now leverage the following three equations

$$q = \frac{\bar{L} - L}{F} \quad (A.10)$$

$$1 - q = \frac{V - \bar{V}}{F} \quad (A.11)$$

$$Fz = Bx_B + Dx_D \quad (A.12)$$

Noting that A.12 can be rearranged as

$$z = \frac{Bx_B + Dx_D}{F} \quad (A.13)$$

Now, substituting A.10, A.11, and A.13 into A.9, we get

$$y = \left( q \cdot \frac{-1}{1-q} \right) x - \left( \frac{-1}{1-q} \cdot z \right)$$

Which simplifies to

$$y = \frac{q}{q-1} + \frac{z}{1-q} \quad (2.19)$$

□

#### A.4. Transfer Unit Analysis Equation

This is a proof of Equation 3.10. Given the flux equation

$$N_A = k_y(y_i - y) \quad (A.14)$$

We can multiply both sides of the expression by  $aA_c dz$  which yields

$$N_A a A_c dz = k_y(y_i - y) a A_c dz \quad (A.15)$$

But, since

$$N_A a A_c dz = V dy_A \quad (A.16)$$

We can combine A.15 and A.16

$$k_y(y_i - y) a A_c dz = V dy_A$$

And rearranging for  $dz$  we get

$$dz = \frac{V dy_A}{k_y(y_i - y) a A_c}$$

Setting up an integral from the bottom to the top of this column section we get

$$\int_0^{h_e} dz = \frac{V}{k_y a A_c} \int_{y_{in,e}}^{y_{out,e}} \frac{dy_A}{(y_i - y)}$$

And integrating the left side we get

$$h_e = \frac{V}{k_y a A_c} \int_{y_{in,e}}^{y_{out,e}} \frac{dy_A}{(y_i - y)} \quad (3.10)$$

□