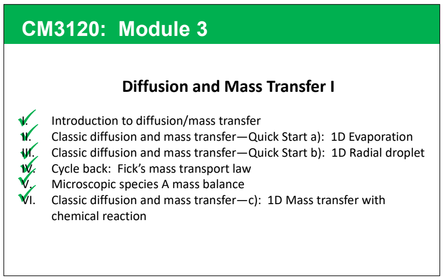
✓Module 3
(done)



CM3120: Module 3

Diffusion and Mass Transfer I

✓ I. Introduction to diffusion/mass transfer
✓ II. Classic diffusion and mass transfer—Quick Start a): 1D Evaporation
✓ III. Classic diffusion and mass transfer—Quick Start b): 1D Radial droplet
✓ IV. Cycle back: Fick's mass transport law
✓ V. Microscopic species A mass balance
✓ VI. Classic diffusion and mass transfer—c): 1D Mass transfer with chemical reaction

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Module 4: Take Stock

Unit Operations

Ref: https://www.sciencehistory.org/historical-profile/arthur-d-little-william-h-walker-and-warren-k-lewis

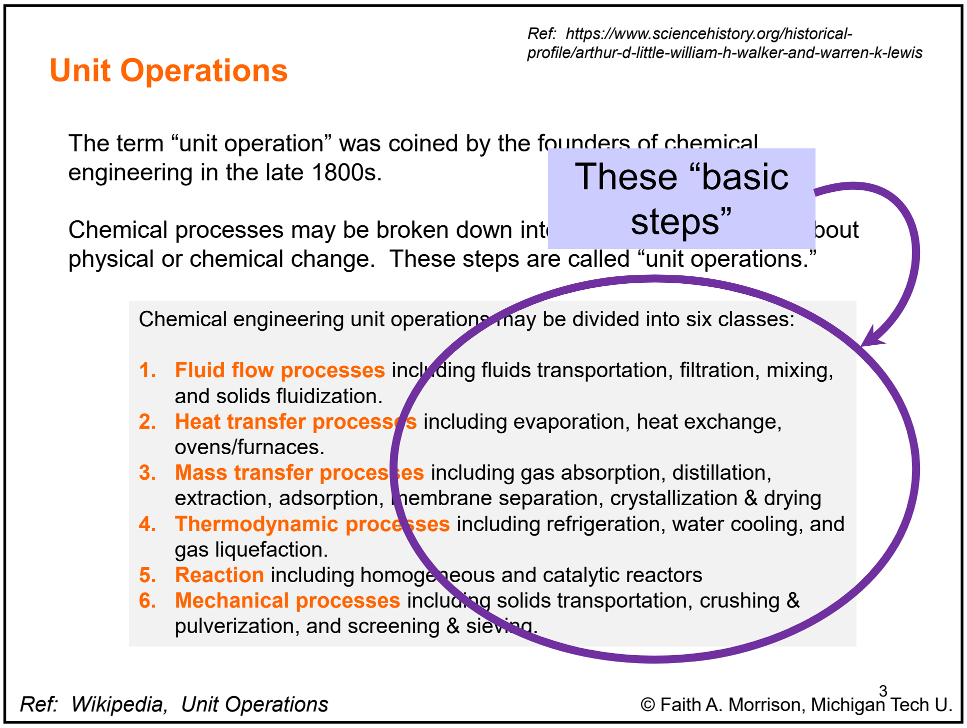
The term "unit operation" was coined by the founders of chemical engineering in the late 1800s.

Chemical processes may be broken down into basic steps that bring about physical or chemical change. These steps are called "unit operations."

Chemical engineering unit operations may be divided into six classes:

1. **Fluid flow processes** including fluids transportation, filtration, mixing, and solids fluidization.
2. **Heat transfer processes** including evaporation, heat exchange, ovens/furnaces.
3. **Mass transfer processes** including gas absorption, distillation, extraction, adsorption, membrane separation, crystallization & drying
4. **Thermodynamic processes** including refrigeration, water cooling, and gas liquefaction.
5. **Reaction** including homogeneous and catalytic reactors
6. **Mechanical processes** including solids transportation, crushing & pulverization, and screening & sieving.

Ref: Wikipedia, Unit Operations



Ref: *https://www.sciencehistory.org/historical-profile/arthur-d-little-william-h-walker-and-warren-k-lewis*

Unit Operations

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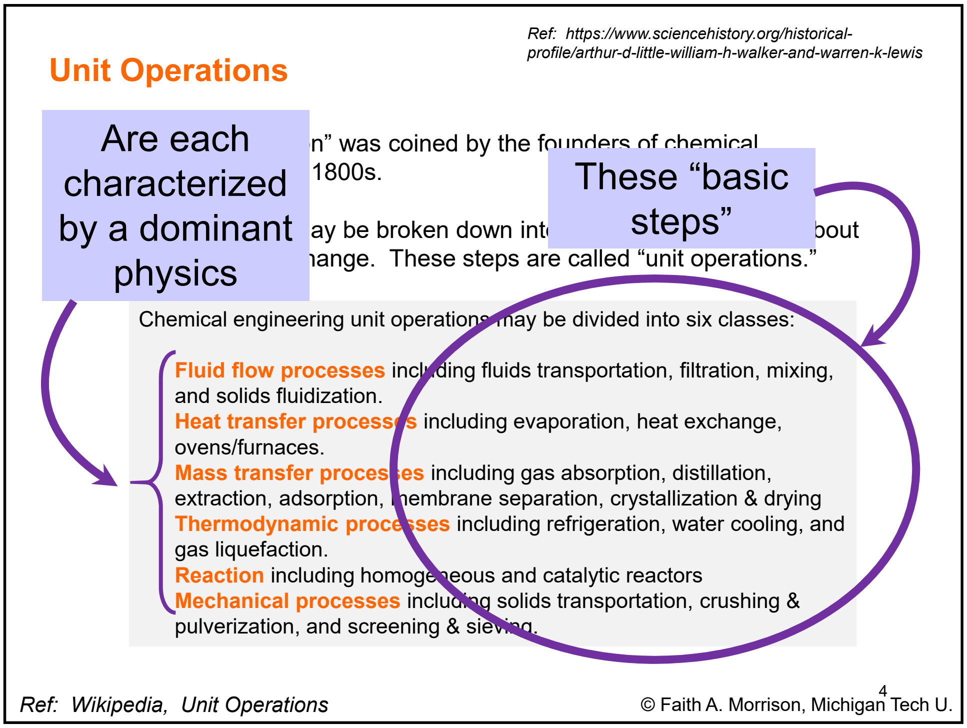
Ref: *Wikipedia, Unit Operations*



Ref: *https://www.sciencehistory.org/historical-profile/arthur-d-little-william-h-walker-and-warren-k-lewis*

Unit Operations

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ay be broken down int bout hange. These steps are called “unit operations.”

Are each characterized by a dominant physics

These “basic steps”

Chemical engineering unit operations may be divided into six classes:

- **Fluid flow processes** including fluids transportation, filtration, mixing, and solids fluidization.
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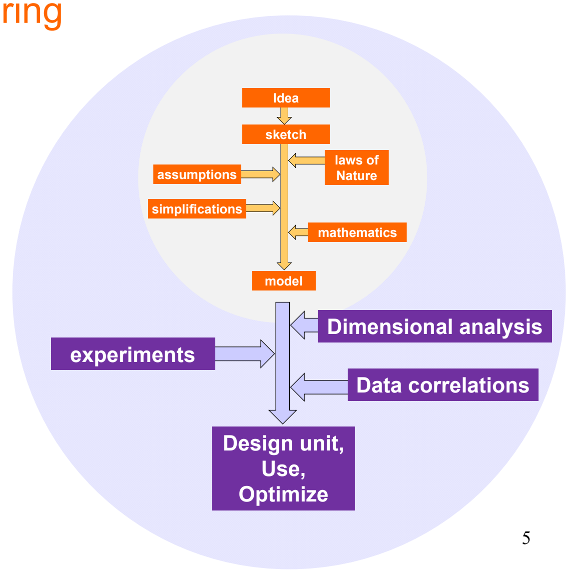
- **Reaction** including homogeneous and catalytic reactors
- **Mechanical processes** including solids transportation, crushing & pulverization, and screening & sieving.

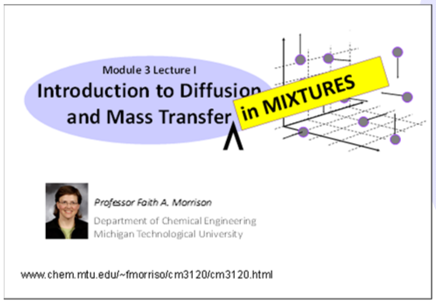
Ref: *Wikipedia, Unit Operations*

Pulling together the physics (how the world works) for these units is the subject of the field of chemical engineering


Idea
sketch
assumptions
laws of Nature
simplifications
mathematics
model
experiments
Dimensional analysis
Data correlations
Design unit, Use, Optimize

Let’s get specific

How does this process work for units dominated by mass transfer?

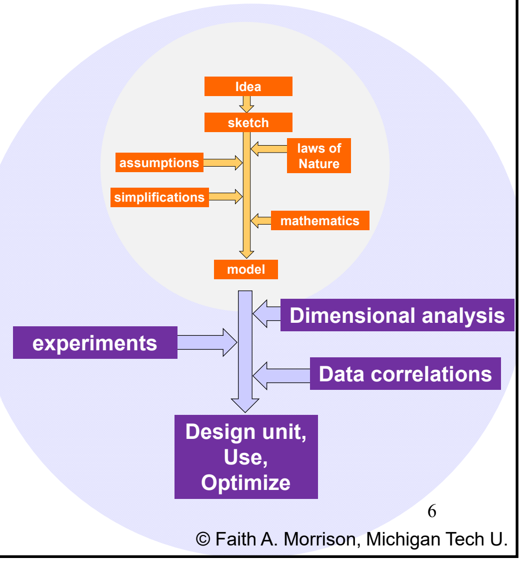

Module 3 Lecture I

Introduction to Diffusion and Mass Transfer ^ in MIXTURES

Professor Faith A. Morrison
Department of Chemical Engineering
Michigan Technological University

www.chem.mtu.edu/~fmorriso/cm3120/cm3120.html

Process for pulling the physics together for a unit


Idea
sketch
assumptions
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simplifications
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Dimensional analysis
Data correlations
Design unit, Use, Optimize

Species A Mass Transfer Processes

Engineering Purposes:

- **Distillation**
- **Gas absorption**
- **Extraction**
- **Membrane separation**

Knowledge and Skills

1. Continuum, mixtures
2. Mass, species A mass, energy balances, fluid flow fundamentals
3. Species A flux ∝ concentration gradient
4. Transfers at boundaries, k_x
5. Dimensional analysis and data correlations $\mathrm{Nu}_{AB}, \mathrm{Sh}$
6. Thermo: Binary phase equilibria
7. Classics: Stagnant layers, constant molar overflow, equimolar counter diffusion, film model, penetration model, boundary layers

---

Species A Mass Transfer Processes

Engineering Purposes:

- **Distillation**
- **Gas absorption**
- **Extraction**
- **Membrane separation**

Modules 3, 4 will cover these topics for species A mass transfer

Knowledge and Skills

1. Continuum, mixtures
2. Mass, species A mass, energy balances, fluid flow fundamentals
3. Species A flux ∝ concentration gradient
4. Transfers at boundaries, k_x
5. Dimensional analysis and data correlations $\mathrm{Nu}_{AB}, \mathrm{Sh}$
6. Thermo: Binary phase equilibria
7. Classics: Stagnant layers, constant molar overflow, equimolar counter diffusion, film model, penetration model, boundary layers

Species A Mass Transfer Processes

Module 3 **Module 4** **Friday Project**

Knowledge and Skills

1. Continuum, mixtures
2. Mass, species A mass, *micro/macro, unsteady* energy balances, fluid flow fundamentals
3. Species A flux $\propto$ concentration gradient
4. Transfers at boundaries, k_x
5. Dimensional analysis and data correlations $\mathrm{Nu}_{AB}, \mathrm{Sh}$
6. Thermo: Binary phase equilibria
7. Classics: Stagnant layers, constant molar overflow, equimolar counter diffusion, film model, penetration model, boundary layers

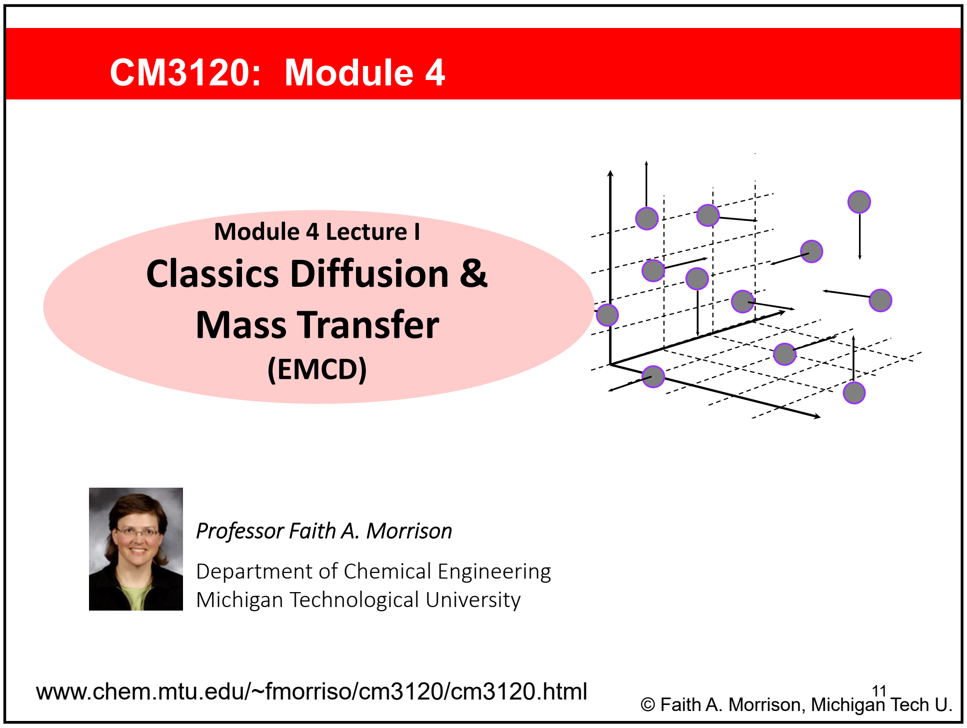
Engineering Purposes:

- Distillation—CMO
- Gas absorption—penetration model
- Extraction
- Membrane separation

CM3120: Module 4

Diffusion and Mass Transfer II

I. Classic diffusion and mass transfer: d) EMCD
II. Classic diffusion and mass transfer: e) Penetration model
III. Unsteady macroscopic species A mass balances (Intro)
IV. Interphase species A mass transfers—To an interface—k_x, k_c, k_p
V. Unsteady macroscopic species A mass balances (Redux)
VI. Interphase species A mass transfers—Across multiple resistances—K_L, K_G
VII. Dimensional analysis
VIII. Data correlations



CM3120: Module 4

Module 4 Lecture I

Classics Diffusion & Mass Transfer

(EMCD)

Professor Faith A. Morrison

Department of Chemical Engineering
Michigan Technological University

www.chem.mtu.edu/~fmorriso/cm3120/cm3120.html

Classic 1D Steady Diffusion Summary

a. 1D rectangular mass transfer (evaporating tank, **Ex 1**)

b. 1D radial mass transfer (evaporating droplet, **Ex 2**)

c. Heterogeneous chemical reaction (catalytic converter, **Ex 3**)

d.

Introduction to Diffusion and Mass Transfer in Mixtures

QUICK START

Recurring Modeling Assumptions in Diffusion ("Classics")

- Near a liquid-gas interface, the region in the gas near the liquid is a film where slow diffusion takes place
- The vapor near the liquid-gas interface is often saturated (Raoult's law, $x_A = p_A^*/p$)
- If component A has no sink, flux $\underline{N}_A = 0$.
- If A diffuses through stagnant B, $\underline{N}_B = 0$.
- If A is dilute in B, we can neglect the convection term ($N_{Az} = J_{Az}^*$)
- Because diffusion is slow, we can make a quasi-steady-state assumption
- If, for example, two moles of A diffuse to a surface at which a rapid, irreversible reaction coverts it to one mole of B, then at steady state $-0.5\underline{N}_A = \underline{N}_B$.
- Homogeneous reactions appear in the mass balance; heterogeneous reactions appear in the boundary conditions and relate fluxes
- If a binary mixture of A and B are undergoing steady equimolar counter diffusion, $\underline{N}_A = -\underline{N}_B$. (coming)

1D Steady Diffusion

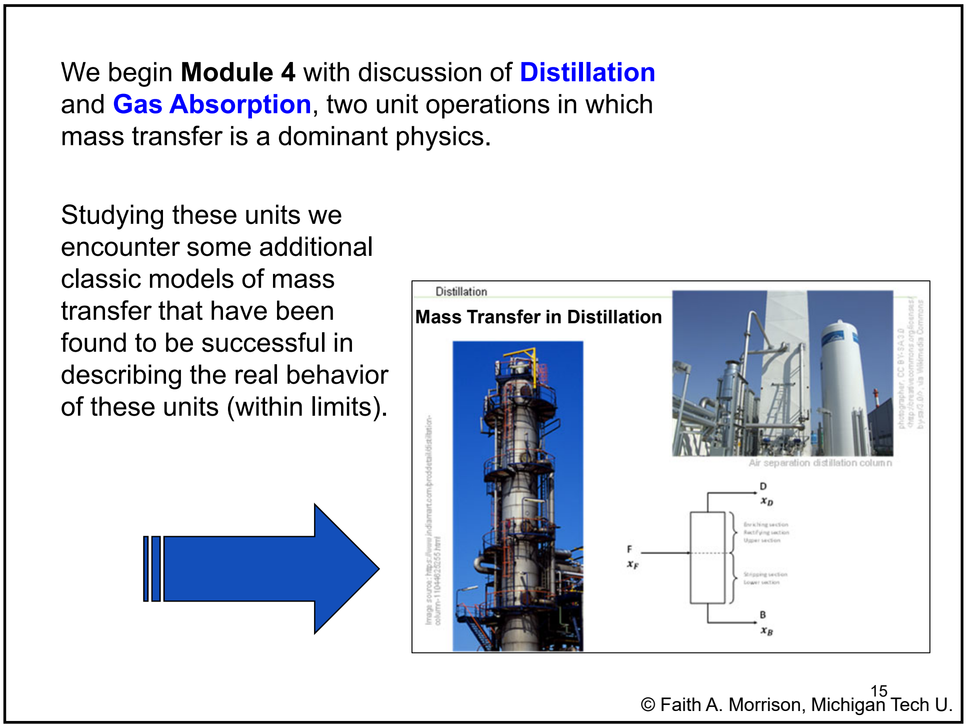
Classic 1D Steady Diffusion Summary

a. 1D rectangular mass transfer (evaporating tank, **Ex 1**)

b. 1D radial mass transfer (evaporating droplet, **Ex 2**)

c. Heterogeneous chemical reaction (catalytic converter, **Ex 3**)

Next: ➡ d. Equimolar counter diffusion (distillation, $\underline{v}^* = 0,\ (\underline{N}_A = \underline{J}_A^*)$ **Ex 4**)



We begin **Module 4** with discussion of **Distillation** and **Gas Absorption**, two unit operations in which mass transfer is a dominant physics.

Studying these units we encounter some additional classic models of mass transfer that have been found to be successful in describing the real behavior of these units (within limits).

Distillation

Mass Transfer in Distillation

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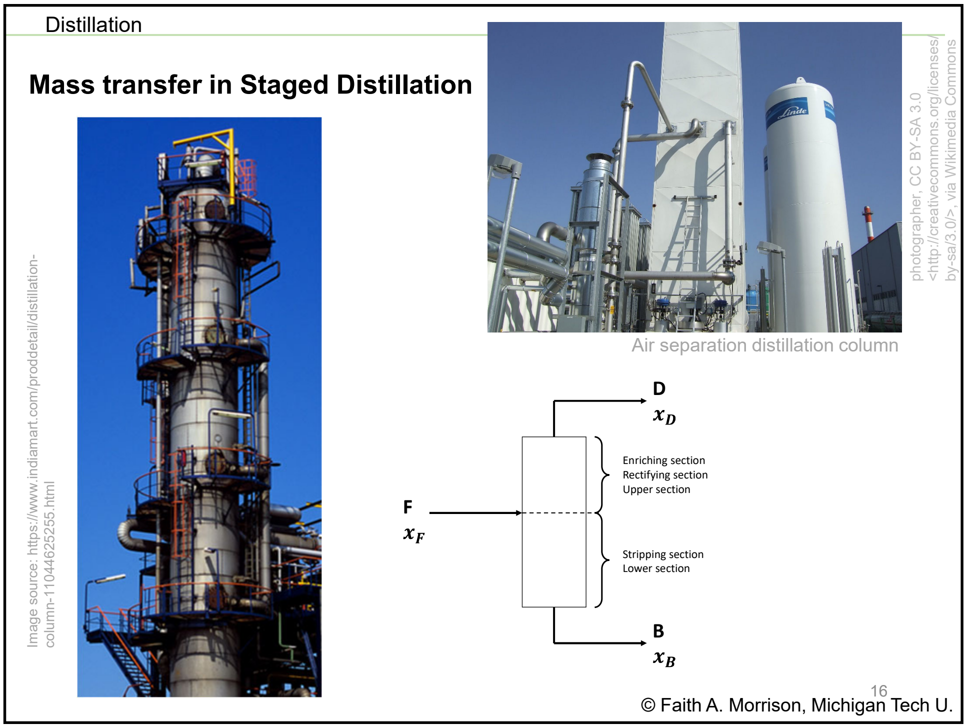

Distillation

Mass transfer in Staged Distillation

Image source: https://www.indiamart.com/proddetail/distillation-column-11044625255.html

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Air separation distillation column

© Faith A. Morrison, Michigan Tech U.

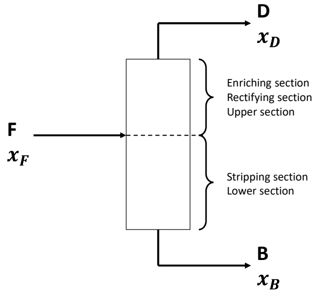
Distillation

Distillation is the process of separating the components of a liquid mixture by exploiting differences in the relative volatility of the mixture's components.

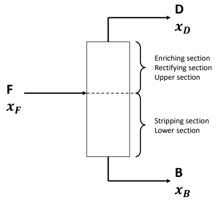
The classic separation produces a **distillate stream** (at the top) that is rich in the component with lower boiling point (higher volatility) and a **bottoms stream** that is rich in the component with higher boiling point (lower volatility).

In a distillation, column, because the components are *vaporized*, distillation is energy-intensive (expensive).

Distillation is the most common unit operation.



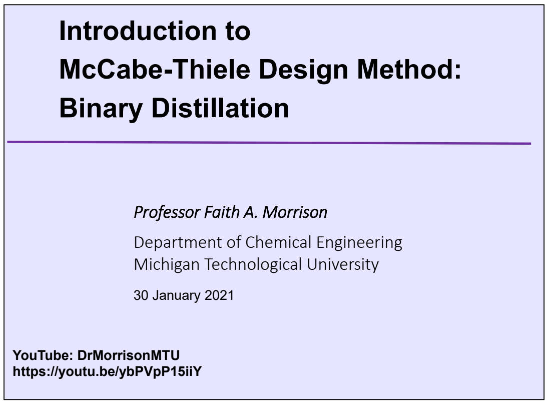
REVIEW



A simplified model of **staged distillation** produces the McCabe-Thiele method of designing (sizing) distillation columns

(See YouTube video on my channel, Dr.MorrisonMTU)

(separations course)



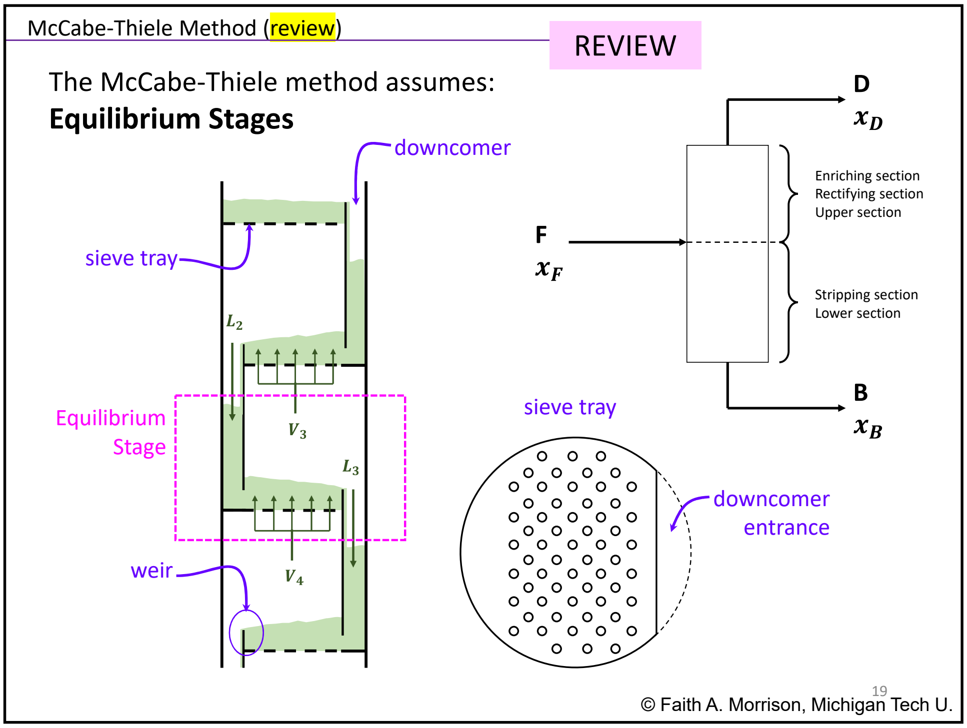
Introduction to McCabe-Thiele Design Method: Binary Distillation

Professor Faith A. Morrison

Department of Chemical Engineering
Michigan Technological University

30 January 2021

YouTube: DrMorrisonMTU
https://youtu.be/ybPVpP15iiY

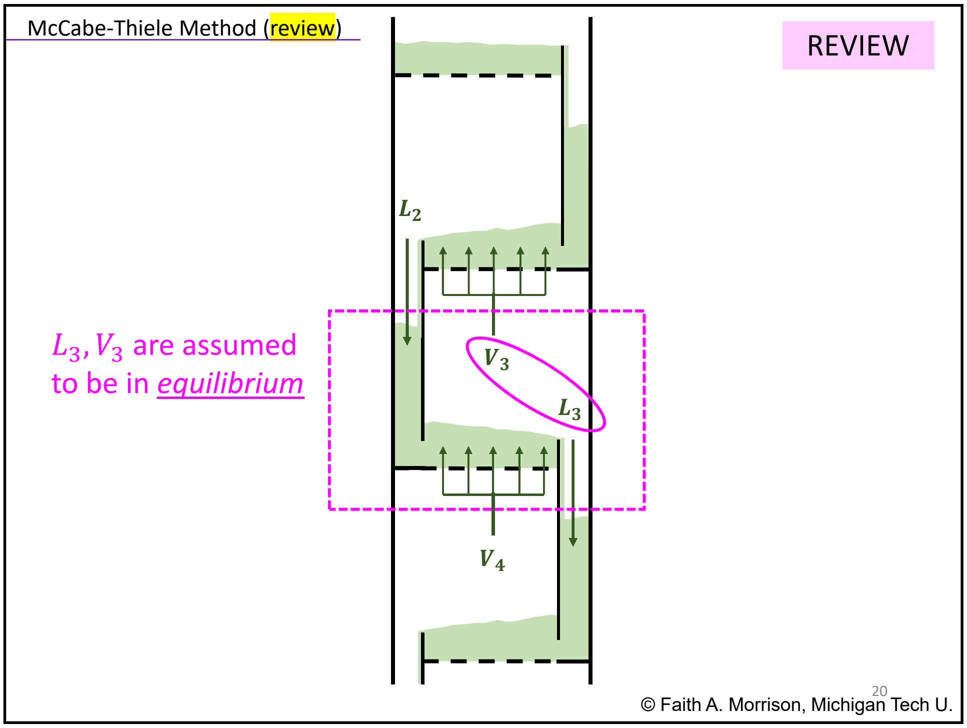


McCabe-Thiele Method (review)

REVIEW

The McCabe-Thiele method assumes:

Equilibrium Stages



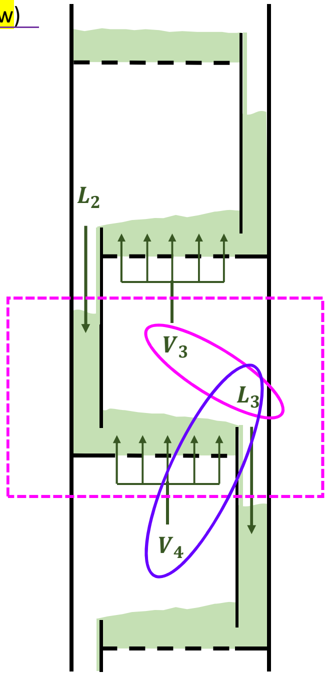
McCabe-Thiele Method (review)

REVIEW

L_3, V_3 are assumed to be in *equilibrium*

McCabe-Thiele Method (review)

REVIEW



L_3, V_3 are assumed to be in *equilibrium*

L_3, V_4 are *passing streams* linked by the operating line (mass balance on upper half of column)

McCabe-Thiele Method (review)

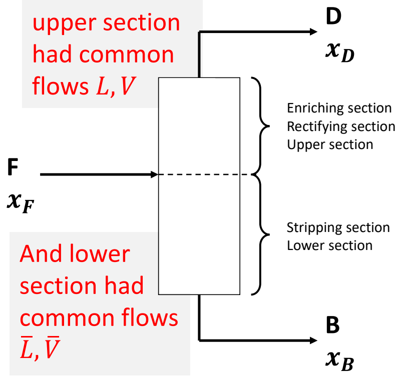
REVIEW

The McCabe-Thiele method assumes:

Constant Molar Overflow (CMO)

Enriching section
Liquid molar flow rates $= L$
Vapor molar flow rates $= V$

Stripping section
Liquid molar flow rates $= \bar{L}$
Vapor molar flow rates $= \bar{V}$



We assumed upper section had common flows L, V

And lower section had common flows $\bar{L}, \bar{V}$

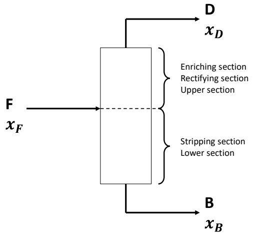
Four conditions:
1. $\Delta\hat{H}_{vap}$ independent of mixture concentration
2. Latent heat dominates
3. Adiabatic column, $\dot{Q} = 0$
4. Saturated liquid and vapor lines on $\hat{H} - x_A$ diagram are parallel

These assumptions have mass transfer implications

McCabe-Thiele Method (review)

REVIEW

McCabe-Thiele method



Goal: Determine the number of stages of a distillation column that can achieve the desired separation

Constraints

1. Overall mass conservation (mole balances)
2. Equilibrium stages
3. All stages above the feed satisfy the same mole balances drawn through D
4. All stages below the feed satisfy the same mole balances drawn through B
5. Upper and lower operating lines intersect at the feed tray
6. The quality q of the feed and mole balances on each phase at the feed tray close the calculation

---

McCabe-Thiele Method (review)

REVIEW

Summary of Constraints—McCabe-Thiele method

1. Overall mass conservation (mole balances)

$$F = D + B$$

$$x_F F = x_D D + x_B B$$

2. Equilibrium stages: data $y^* = f(x^*)$
3. Above the feed mole balances through D constrain passing streams $y(x)$ (upper operating line):

$$y = \left(\frac{L}{V}\right)x + \left(1 - \frac{L}{V}\right)x_D$$

4. Below the feed mole balances through B constrain passing streams $\bar{y}(\bar{x})$ (lower operating line)

$$\bar{y} = \left(\frac{\bar{L}}{\bar{V}}\right)\bar{x} - \left(\frac{\bar{L}}{\bar{V}} - 1\right)x_B$$

5. Upper and lower intersect at feed tray, $\tilde{y}(\tilde{x})$

$$\tilde{y} = \left(\frac{L - \bar{L}}{V - \bar{V}}\right)\tilde{x} + \frac{x_F F}{V - \bar{V}}$$

6. The quality q of the feed and mole balances on each phase at the feed tray close the calculation (q-line)

$$\tilde{y} = \left(\frac{q}{q - 1}\right)\tilde{x} + \frac{x_F}{1 - q}$$

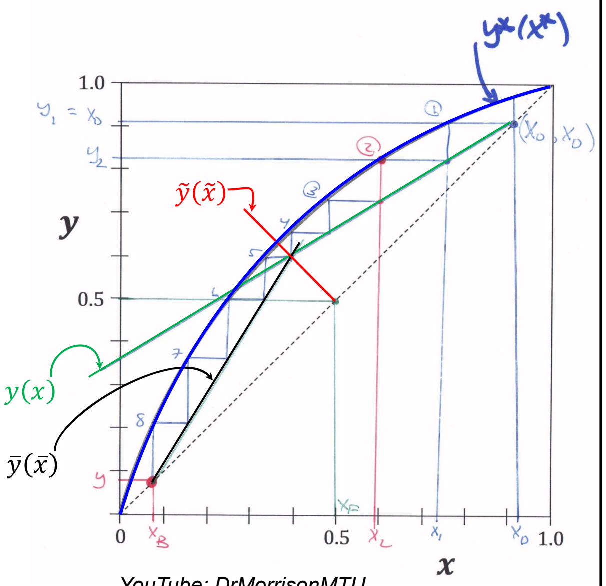
We assume upper section has common flows L, V

And lower section has common flows $\bar{L}, \bar{V}$

McCabe-Thiele Method (review)

REVIEW

The total condenser starts the column calculation with an *equilibrium stage*; the information then passes to the *passing streams* (upper operating line), and then to the next equilibrium stage, etc. alternating until the feed is passed. At this point the passing streams are designated by the lower operating line, and the process continues until the bottoms composition is reached.



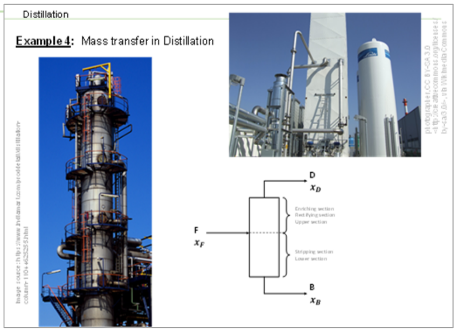
YouTube: DrMorrisonMTU
https://youtu.be/ybPVpP15iiY

Mass Transfer in Distillation

Mass transfer in Distillation

In general, the molar flow rates throughout the enriching (L, V) and stripping $(\bar{L}, \bar{V})$ sections are not constant.

We can assume they are constant if every time a mole of vapor is condensed, a mole of liquid is vaporized (*Constant Molal Overflow*)



Distillation

Example 4: Mass transfer in Distillation

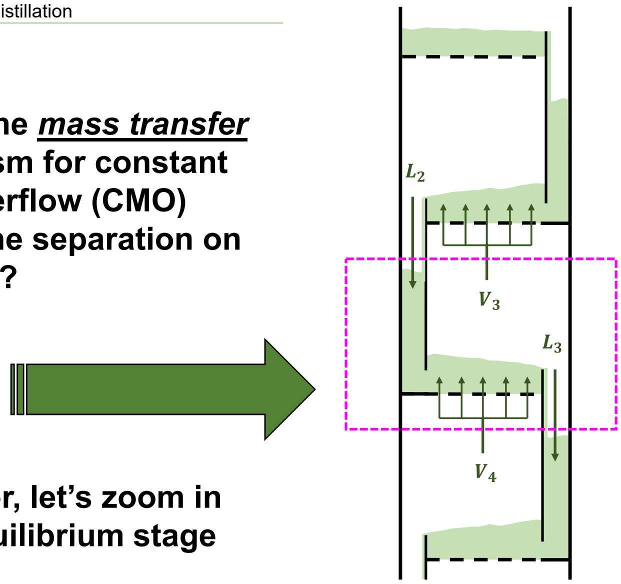
Constant Molal Overflow (CMO), used in McCabe-Thiele method

1. The heat of vaporization per mole $\Delta\hat{H}_{vap} = \lambda$ is constant (independent of concentration)
2. Specific heat changes are small compared to latent heat changes
3. The column is adiabatic, $\dot{Q} = 0$
4. (equivalent to 1+2) The saturated liquid and vapor lines on an enthalpy-composition diagram (in molar units) are parallel

Wankat, pp110-1

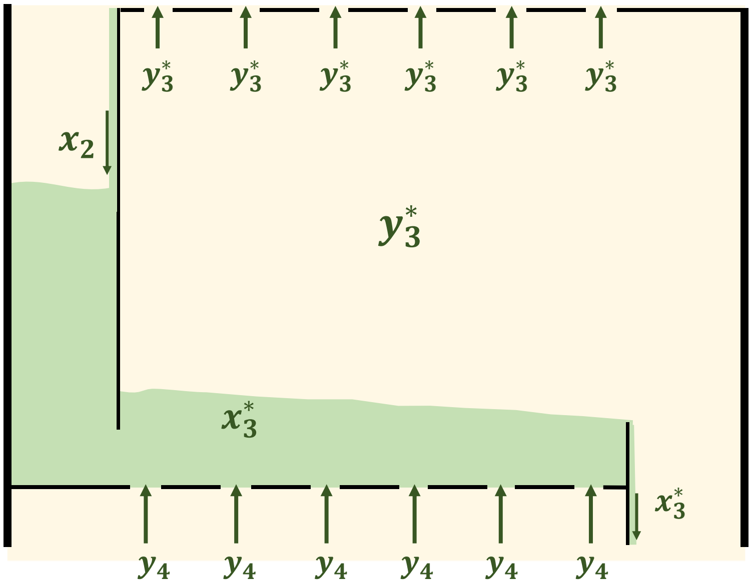
Mass Transfer in Distillation

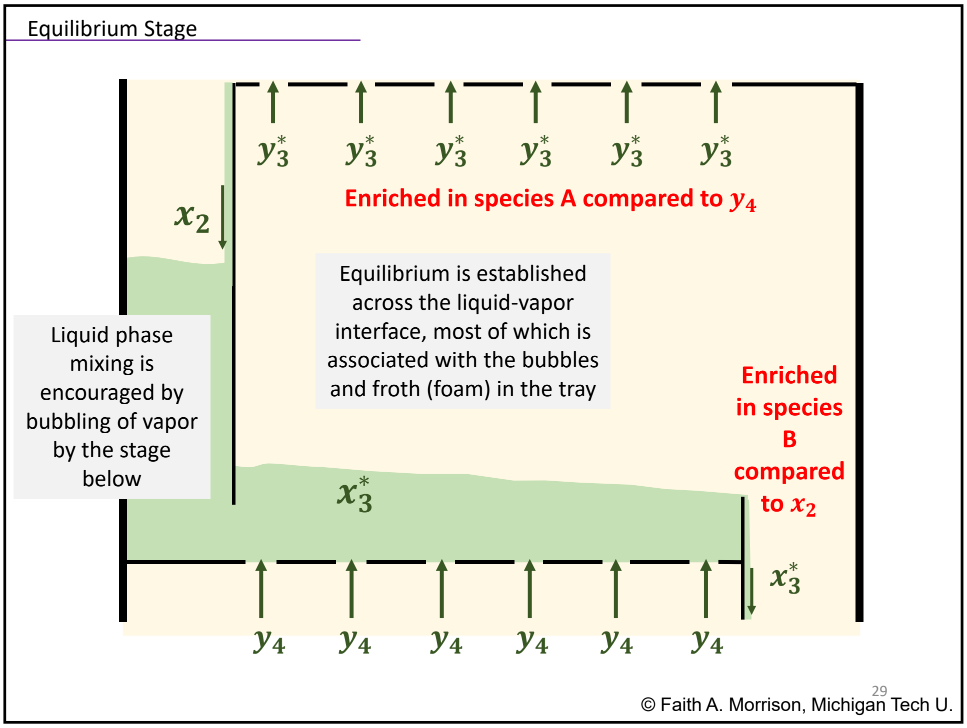
What is the *mass transfer* mechanism for constant molal overflow (CMO) and for the separation on the stage?



To answer, let's zoom in on an equilibrium stage

Equilibrium Stage





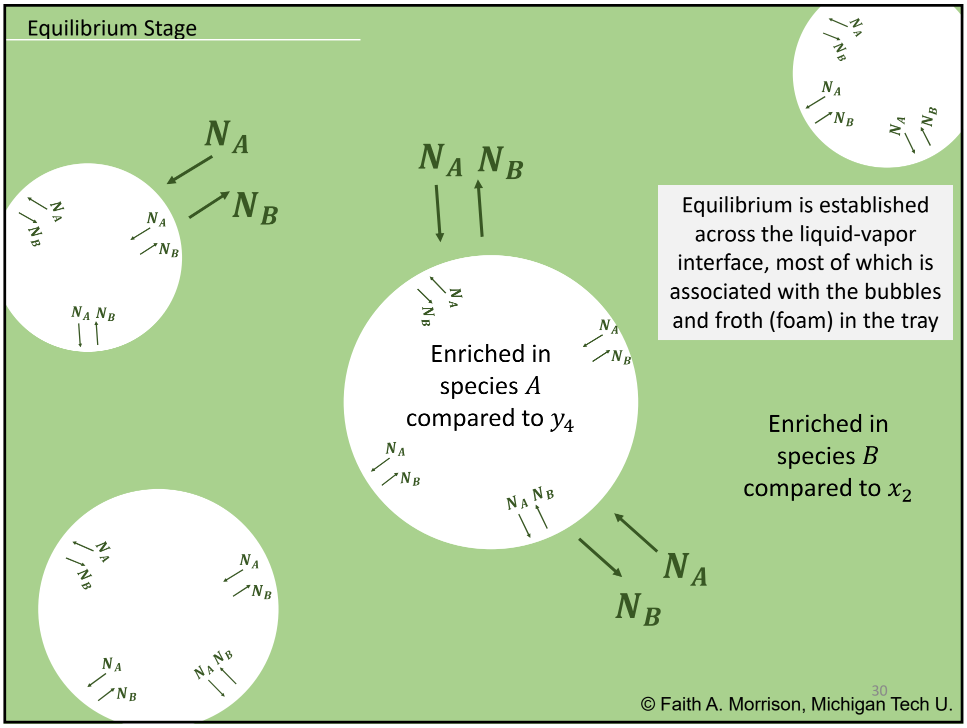
Equilibrium Stage

Enriched in species A compared to y_4

Equilibrium is established across the liquid-vapor interface, most of which is associated with the bubbles and froth (foam) in the tray

Liquid phase mixing is encouraged by bubbling of vapor by the stage below

Enriched in species B compared to x_2



Equilibrium Stage

Equilibrium is established across the liquid-vapor interface, most of which is associated with the bubbles and froth (foam) in the tray

Enriched in species A compared to y_4

Enriched in species B compared to x_2

Mass Transfer in Distillation

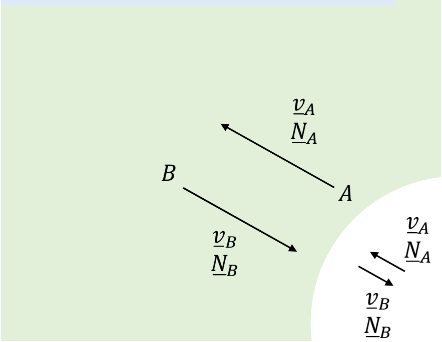
A Picture of Mass Transfer in Distillation

(Mod 3, lecture I)
Diffusion progresses at a rate of
- $\sim 5 cm/min$ (gases)
- $\sim 0.05 cm/min$ (liquids)
- $\sim 10^{-5} cm/min$ (solids)

The molar flow rates throughout the enriching (L, V) and stripping $(\bar{L}, \bar{V})$ sections are constant if:

Every time a mole of vapor is condensed, a mole of liquid is vaporized (**Constant Molal Overflow**)

This condition is met by **equimolar counter diffusion (EMCD)**.



$$\underline{v}_A = -\underline{v}_B$$

$$\underline{N}_A = -\underline{N}_B$$

Note:
$$\underline{N}_A + \underline{N}_B = c\underline{v}^*$$
$$\Rightarrow \underline{v}^* = 0$$

WRF, p499

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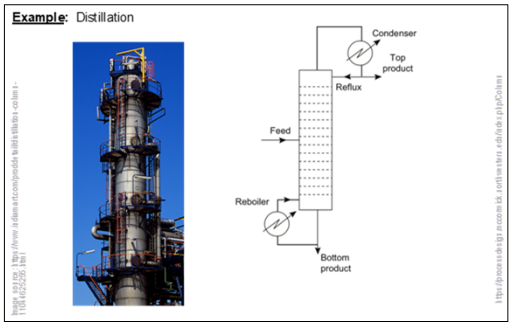
Mass transfer in Distillation

Example 4: Mass transfer in distillation

Equimolar Counter Diffusion



A distillation column is separating two components A and B at steady state. In the vapor phase of each equilibrium stage the two components are moving in **equimolar counter diffusion**. What are the molar fluxes of A and B in the vapor phase? What is the concentration distribution in the region of the equimolar counter diffusion?

Wankat, pp110-1

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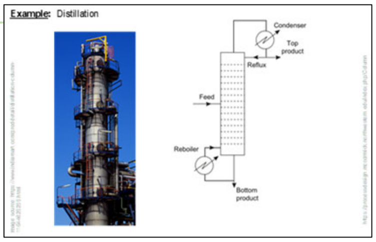
Mass transfer in Distillation

Example 4: Mass transfer in distillation



A distillation column is separating two components A and B at steady state. In the vapor phase of each equilibrium stage the two components are moving in equimolar counter diffusion. What are the molar fluxes of A and B in the vapor phase? What is the concentration distribution in the region of the equimolar counter diffusion?

Solve

See hand notes for the start (Example 4)

HW4 Prob 2 (&7)

Wankat, pp110-1

Mass Transfer in Distillation

Example 4: Mass transfer in distillation

A distillation column is separating two components A and B at steady state. In the vapor phase of each equilibrium stage the two components are moving in equimolar counter diffusion. What are the molar fluxes of A and B in the vapor phase? What is the concentration distribution in the region of the equimolar counter diffusion?

Answers:

$$N_{Az} = \frac{P_{A1} - P_{A2}}{(z_2 - z_1)}\left(\frac{\mathcal{D}_{AB}}{RT}\right)$$

(constant flux proportional to $\mathcal{D}_{AB}$)

$$\frac{x_A - x_{A1}}{x_{A1} - x_{A2}} = \frac{z - z_1}{z_1 - z_2}$$

(linear concentration profile)

$$x_A = \left(\frac{x_{A1} - x_{A2}}{z_1 - z_2}\right) z - \frac{z_1 (x_{A1} - x_{A2})}{z_1 - z_2} + x_{A1}$$

Wankat, pp110-1

1D Steady Diffusion—Equimolar Counter Diffusion

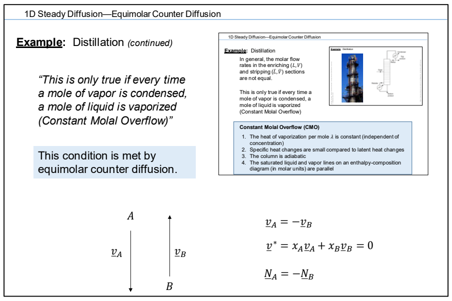
Problem Summary: Equimolar Counter Diffusion (EMCD)

- One-dimensional (1D)
- Steady
- Use molar flux (due to equimolar counter diffusion specified)
- Use combined molar flux $\underline{N}_A$ or $\underline{J}_A^*$
- Boundary conditions: concentrations known over a known distance

Flux choice

Choose:

- **Molar** because equi*molar* motion was specified
- **Combined molar** and **molar** are the same when $\underline{v}^* = 0$ $(\underline{N}_A = \underline{J}_A^*)$



1D Steady Diffusion—Equimolar Counter Diffusion

Example: Distillation *(continued)*

"This is only true if every time a mole of vapor is condensed, a mole of liquid is vaporized (Constant Molal Overflow)"

This condition is met by equimolar counter diffusion.

1D Steady Diffusion—Equimolar Counter Diffusion

Example: Distillation

In general, the molar flow rates in the enriching (L, V) and stripping $(\bar{L}, \bar{V})$ sections are not equal.

This is only true if every time a mole of vapor is condensed, a mole of liquid is vaporized (Constant Molal Overflow)

Constant Molal Overflow (CMO)

1. The heat of vaporization per mole λ is constant (independent of concentration)
2. Specific heat changes are small compared to latent heat changes
3. The column is adiabatic
4. The saturated liquid and vapor lines on an enthalpy-composition diagram (in molar units) are parallel

$\underline{v}_A = -\underline{v}_B$

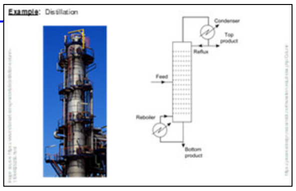
$\underline{v}^* = x_A \underline{v}_A + x_B \underline{v}_B = 0$

$\underline{N}_A = -\underline{N}_B$

$$\underline{J}_A^* = c x_A (\underline{v}_A - \underline{v}^*)$$
$$\underline{N}_A = c_A \underline{v}_A$$

These two molar fluxes are the same when $\underline{v}^* = 0$.

1D Steady Diffusion—Equimolar Counter Diffusion



Analysis:

Assuming EMCD for staged distillation implies linear concentration profile. And constant flux proportional to the diffusion coefficient

$$N_{Az} = \frac{P_{A1} - P_{A2}}{(z_2 - z_1)} \frac{\mathcal{D}_{AB}}{RT}$$

Since $\mathcal{D}_{AB}$ is a ***material property*** of the AB pair, we can easily predict how a new distillation separation will perform (according to the proposed model, i.e. EMCD; but is it true?)

When we make a prediction, the next thing is to check and see if it is true. (Is the tray flux proportional to the diffusion coefficient? It's hard to measure the flux.)

Later we will define some macroscopic mass transfer methods that we can use to assess the degree to which EMCD seems consistent with measurements for distillation (mass transfer coefficients and how they depend on $\mathcal{D}_{AB}$).

For now, we can just hold onto EMCD as an idea of how mass transfer works in a distillation column.

Mass Transfer in Distillation

How good are our modeling assumptions?

Mole fraction of A separated and sent up the column (equilibrium tray): $y_3^* - y_4$. This represents a likely overestimate of the amount of separation achieved.

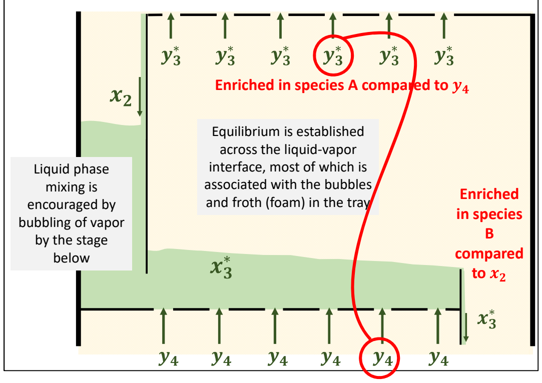
If the tray is not at equilibrium, $y_3 < y_3^*$

Tray efficiency $\equiv \frac{y_3 - y_4}{y_3^* - y_4}$

Murphree efficiency

The *tray efficiency* is an issue of the mass transfer limitations in the separations process taking place.

Equilibrium Stage



Enriched in species A compared to y_4

Equilibrium is established across the liquid-vapor interface, most of which is associated with the bubbles and froth (foam) in the tray

Liquid phase mixing is encouraged by bubbling of vapor by the stage below

Enriched in species B compared to x_2

(We'll return to this efficiency once we develop some more practical mass-transfer tools)

1D Steady Diffusion

Classic 1D Steady Diffusion Summary

a. 1D rectangular mass transfer (evaporating tank, **Ex 1**)

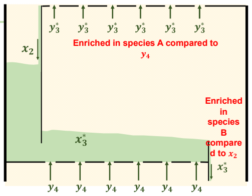
b. 1D radial mass transfer (evaporating droplet, **Ex 2**)

c. Heterogeneous chemical reaction (catalytic converter, **Ex 3**)

d. Equimolar counter diffusion (distillation, $\underline{v}^* = 0,\ (\underline{N}_A = \underline{J}_A^*)$ **Ex 4**)

e. More…

Distillation modeling: EMCD



Distillation Modeling Summary

- Distillation modeling with **equilibrium stages** gives a plausible picture of the unit operation
- **Equimolar counter diffusion (EMCD)** is the mass transfer picture; this is consistent with constant molar overflow (CMO, McCabe Thiele analysis)
- EMCD is a “classic” of diffusion and mass transfer
- Distillation trays are **unlikely to be at equilibrium**; mass transfer limits the separation taking place on the trays; account for this with a **Murphree efficiency**

- Many (most?) columns these days are packed; we would have to consider a different model for packed columns