

Chapter 1. Course Introduction

WHAT ARE "UNIT OPERATIONS"?

A typical process which a chemical engineer might work with is the production of gasoline from crude oil

process = sequence of "unit operations" (physical changes) + chemical reactors

Any process can be subdivided into a number of steps which are performed in sequence to go from some initial starting material (crude oil, in this case) to some final material (gasoline). For example, we might start by heating the crude oil to lower its viscosity, then pump the oil to the distillation column, where we then separate various components of the crude. A unit operation is one of the steps of this sequence. Usually the term refers to steps intended primarily to perform some physical transformation (as opposed to chemical transformation) of the input stream.

Examples of unit operations:

- heat exchange (change temperature of a stream)
- fluid flow (transportation)
- distillation (separation of mixture into multiple streams which are richer in some components than original)
- evaporation (remove water from liquid)
- humidification (increase water content of gas)
- gas absorption (remove one component of a gas mixture)
- sedimentation (separate solid from liquid)
- classification (divide mixture of particles into different "classes" on the basis of size)

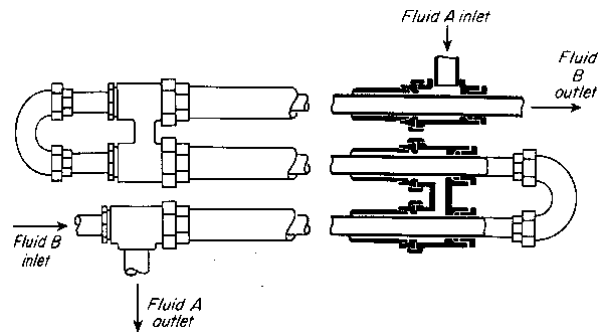
In this course, we will apply the principles learned in the engineering science courses you have had the last three semesters to the design of equipment for physical transformations. We might divide up the courses in the curriculum as follows:

Course	Objective	Scale
Thermo	1) conservation of energy 2) criteria for phase/chemical equilibria	molecular
fluids, heat/mass transfer	rates of physical processes	microscopic
unit operations	design equipment for physical transformations	macroscopic
kinetics	1) rate of chemical processes 2) design equipment for chemical transformations	molecular macroscopic
process design	divide process into sequence of steps (synthesize flowsheet)	supramacro

Chapter 2. Heat Exchange Equipment

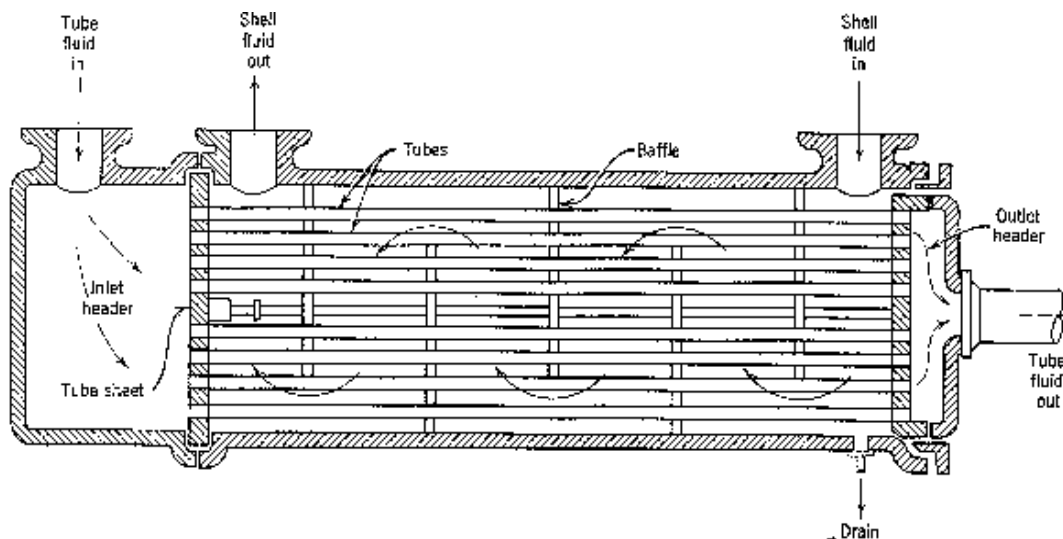
DOUBLE-PIPE HXER

One particularly simple heat-exchange device is the *double-pipe heat exchanger*, shown in the figure at right. It is called this because the basic component is constructed from two pipes, one inside the other. One fluid (Fluid B) flows inside the inner pipe while the second fluid (Fluid A) flows in the annular space between the two pipes. Of course, one fluid is hotter than the other and heat flows through the wall of the inner pipe from the hot fluid to the cold fluid. To obtain larger heat exchange area, several pipes are arranged side-by-side and fittings are attached to allow the fluids to contact the pipes in series so the overall flow is the same as if only one very long pipe were used rather than several shorter ones.



SHELL-AND-TUBE HXER

If very large heat exchange areas are required, the double-pipe heat exchanger design becomes impractical. Instead, the *shell-and-tube heat exchanger* design is used.



Shown above is a bundle of small-diameter tubes which are arranged parallel to each other and reside inside a much larger-diameter tube called the “shell”, much like strands of uncooked spaghetti come in a tube-shaped container. The tubes are all manifolded together at either end so

that the “tube fluid” enters the left side and is distributed equally among all the tubes. At the right side, the fluid exits from each tube, is mixed together in a second manifold, then leaves as a single stream. The second fluid, called the “shell fluid”, flows in the space in between the outside of tubes. Baffle plates inside the shell force the shell fluid to flow across the tubes repeatedly as the fluid moves along the length of the shell.

In the design above (called a 1-1 hxer), the flow is from left to right inside the tubes and from right to left for the shell-side fluid. Another common design is shown below (called a 1-2 hxer).

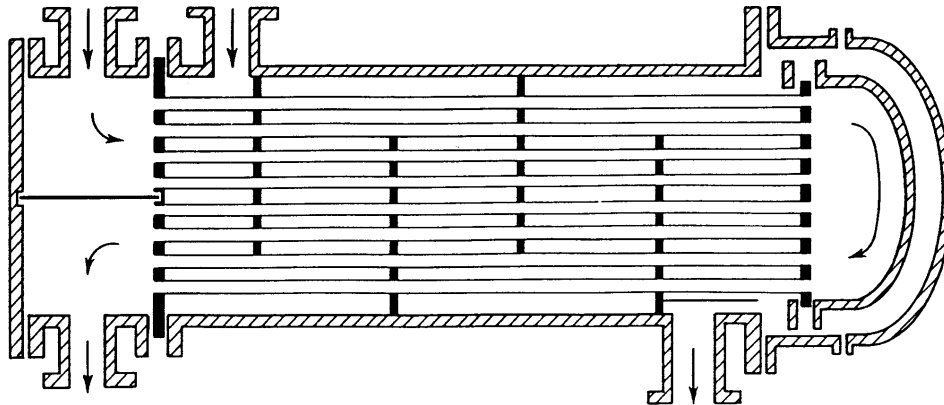


FIGURE 15.3
1-2 parallel-counterflow exchanger.

Half of the tubes have flow from left to right while the other half have flow in the opposite direction.

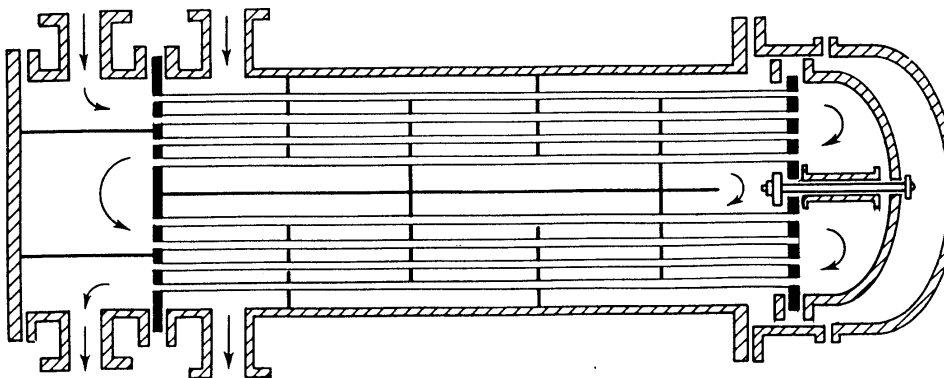


FIGURE 15.4
2-4 exchanger.

Chapter 3. Fundamentals of Heat Transfer: Review

LOG-MEAN DRIVING FORCE

The design equation used for sizing heat exchangers generally takes the form of

$$q = U A \Delta T \quad (1)$$

where q is the heat duty of the exchanger (rate of energy transfer) U is some heat-transfer coefficient, A is the area of the heat exchange surface, and ΔT is the driving force for heat transfer.

In any real heat exchanger, the local driving force ΔT will vary along the length of the exchanger: say it varies between ΔT_1 at one end of the exchanger to ΔT_2 at the other end. Then the question arises: which value of ΔT do you use in (1)? The answer turns out to be: use the *log mean* of ΔT_1 and ΔT_2 :

$$\overline{\Delta T}_L = \frac{\Delta T_1 - \Delta T_2}{\ln \frac{\Delta T_1}{\Delta T_2}}$$

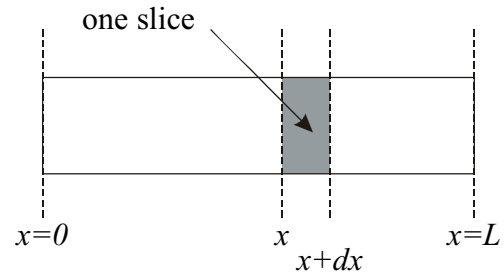
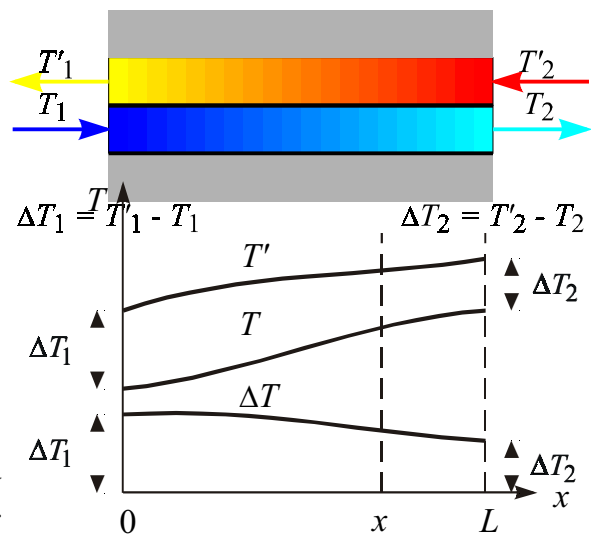
This turns out to be correct in nearly every situation. We will prove it now for one particular case and leave some other cases to be proved in the homework (HWK #1, Probl. 1)

Proof: When the driving force varies with position along the exchanger, the usual approach to math modelling is to divide the length of the hxr (L) into a large number of thin slices, such that the thickness of each slice is thin enough so that the temperature of either stream is essentially constant over the slice, leaving the driving force constant over the slice:

$$\Delta T = T'(x) - T(x)$$

Depending on which x we choose, we get a different driving force. The rate of heat transfer from the hot fluid to the cold fluid in any slice is given by a *local heat transfer coefficient* $U(x)$:

$$dq = U(x) \Delta T(x) dA \quad (2)$$



where $q(x)$ is the rate of heat transferred from the hot fluid to the cold fluid in the length of hxer from $x=0$ and $x=x$; and dq is

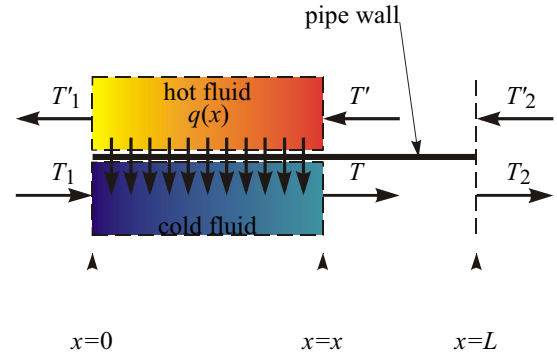
$$q(x+dx) = q(x) + dq$$

and dA is the heat exchange area in this slice of length dx . If the inner pipe (of a double-pipe hxer) is a cylinder of diameter D , then the heat exchange area of this slice is

$$dA = \pi D dx$$

Integrating (2) as a function of x is difficult since we'd have to predict $\Delta T(x)$. There is a easier way (but a "trick" is required). Consider steady-state counter-current flow through a double-pipe heat exchanger (shown at right). A steady-state energy balance on the hot fluid gives

$$\begin{aligned} \text{rate in} &= \text{rate out} \\ m'H' &= m'H'_1 + q \end{aligned} \quad (3)$$



A similar balance on the cold fluid gives

$$\begin{aligned} \text{rate in} &= \text{rate out} \\ mH_1 + q &= mH \end{aligned} \quad (4)$$

$$\text{Solving (3) and (4) for } q: \underbrace{m[H(x) - H_1]}_{\text{rate of energy gained by cold stream}} = q(x) = \underbrace{m'[H'(x) - H'_1]}_{\text{rate of energy lost by hot stream}} \quad (5)$$

where m is the mass flowrate of the stream (units are Kg/sec), H is the enthalpy per unit mass (units are J/Kg), the subscripts and primes have the following meaning:

- unprimed refers to the cold stream,
- prime refers to the hot stream,
- "1" refers to the left end of hxer, and
- "2" refers to the right end of hxer.

Now, let's try to relate each enthalpy to the appropriate temperature. In general, enthalpy changes can have both *latent heat* (caused by change in phase) and *sensible heat* (caused by change in temperature) contributions.

$$dH = \underbrace{c_p dT}_{\text{sensible heat}} + \underbrace{\lambda dy}_{\text{latent heat}}$$

where

- dH is the change in enthalpy (energy/mass)
- c_p is the heat capacity (energy/mass/degree) of the fluid, also known as “specific heat”
- dT is the change in temperature (degree)
- λ is the heat of vaporization (energy/mass)
- dy is the mass fraction of fluid vaporized

When the fluid consists of two phases (liquid and vapor), which have different heat capacities c_{pL} and c_{pV} , we use weighed average of the two heat capacities

$$c_p = (1-y)c_{pL} + y c_{pV}$$

where y is the mass fraction of vapor present and $1-y$ is the mass fraction of liquid present. For the time being, let's assume:

Assumption #1: no phase changes occur in either fluid

Now we only have to worry about contributions from changes in the temperature (sensible heat):

$$dH = c_p dT$$

Integrating over the temperature change allows us to evaluate the change in enthalpy

$$\Delta H = \int_{T_a}^{T_b} c_p dT = c_p (T_b - T_a)$$

using assumption #1 using assumption #2

In general, the specific heat (c_p) depends on temperature. But if the temperature change is not too large — say 10-20° — then the specific heat doesn't change too much. Let's assume we can neglect these small changes:

Assumption #2: constant specific heat for both streams

Then we can factor c_p out of the integral and the integration becomes trivial:

$$\Delta H = c_p \Delta T$$

In particular,

$$H - H_1 = c_p(T - T_1)$$

and

$$H' - H'_1 = c'_p(T' - T'_1)$$

where c_p and c'_p are the specific heats of the cold and hot streams. Thus (5) can be rewritten as:

$$\text{at } x=x: \quad mc_p(T(x) - T_1) = m'c'_p(T'(x) - T'_1) = q(x) \quad (6)$$

For example,

$$\text{at } x=0: \quad mc_p(T_1 - T_1) = m'c'_p(T'_1 - T'_1) = q(0) = 0$$

In particular, we are interested in the total rate of heat transfer over the entire length L of the exchanger:

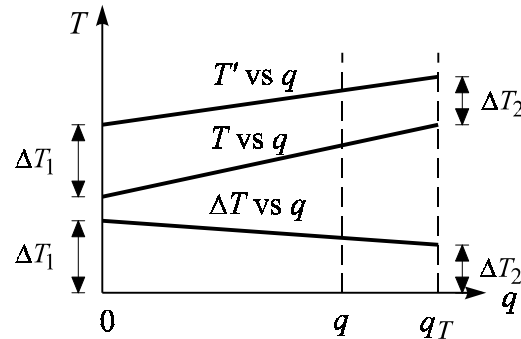
$$\text{at } x=L: \quad mc_p(T_2 - T_1) = m'c'_p(T'_2 - T'_1) = q(L) \equiv q_T$$

Now let me show you the "trick": using (6), I can show that the temperature of either stream [i.e. $T(x)$ or $T'(x)$] is a linear function of the amount of heat transferred, $q(x)$:

$$T(x) = T_1 + \left(\frac{1}{mc_p} \right) q(x)$$

$$T'(x) = T'_1 + \left(\frac{1}{m'c'_p} \right) q(x)$$

Since both temperatures are linear functions of q , their difference is also a linear function of q . A straight line has the very nice property that its slope is the same at every point:



$$\frac{d(\Delta T)}{dq} = \text{const} = \frac{\Delta T_2 - \Delta T_1}{q_T - 0} \quad (7)$$

I can easily evaluate the driving force (ΔT) at the two ends of the heat exchanger, and I know the total heat duty (q_T), so I can calculate this slope. The dq and $d(\Delta T)$ which appear in (7) represent the incremental rate of heat transfer and the change in driving force ΔT which occurred over a different length dx of the heat exchanger (from x to $x+dx$). They are related by

$$dq = U dA \Delta T \quad (8)$$

where dA is the heat exchange area in that slice of the heat exchanger from x to $x+dx$. Treating the heat exchange surface as a cylinder of radius R :

$$dA = 2\pi R dx$$

(8) into (7):

$$\frac{d(\Delta T)}{U(\Delta T)(dA)} = \frac{\Delta T_2 - \Delta T_1}{q_T}$$

or

$$\frac{d(\Delta T)}{\Delta T} = \frac{\Delta T_2 - \Delta T_1}{q_T} U(dA)$$

Next, we integrate over the length of the heat exchanger from $x=0$ (where $\Delta T = \Delta T_1$) to $x=L$ (where $\Delta T = \Delta T_2$):

$$\int_{\Delta T_1}^{\Delta T_2} \frac{d(\Delta T)}{\Delta T} = \frac{\Delta T_2 - \Delta T_1}{q_T} \int_{x=0}^{x=L} U(x) \cdot \underbrace{2\pi R dx}_{dA}$$

The integral on the right-hand-side becomes trivial to evaluate if we can make one additional assumption:

Assumption #3: U is constant

Then we can factor U outside the integral and integrate the remainder:

$$\int_{x=0}^{x=L} 2\pi R dx = 2\pi R \int_0^L dx = 2\pi RL = A_T$$

which is just the total heat exchange area. Thus we have

$$\ln \frac{\Delta T_2}{\Delta T_1} = \frac{\Delta T_2 - \Delta T_1}{q_T} U A_T$$

Solving for the total heat duty

$$q_T = U A_T \frac{\Delta T_2 - \Delta T_1}{\ln \frac{\Delta T_2}{\Delta T_1}}$$

or

$$q_T = U A_T \overline{\Delta T}_L \quad \text{where} \quad \overline{\Delta T}_L = \frac{\Delta T_2 - \Delta T_1}{\ln \frac{\Delta T_2}{\Delta T_1}}$$

is called the **log-mean temperature difference** (LMTD). It represents the average driving force for heat transfer. This result provides us with the main **design equation** for heat exchangers.

Summary of assumptions:

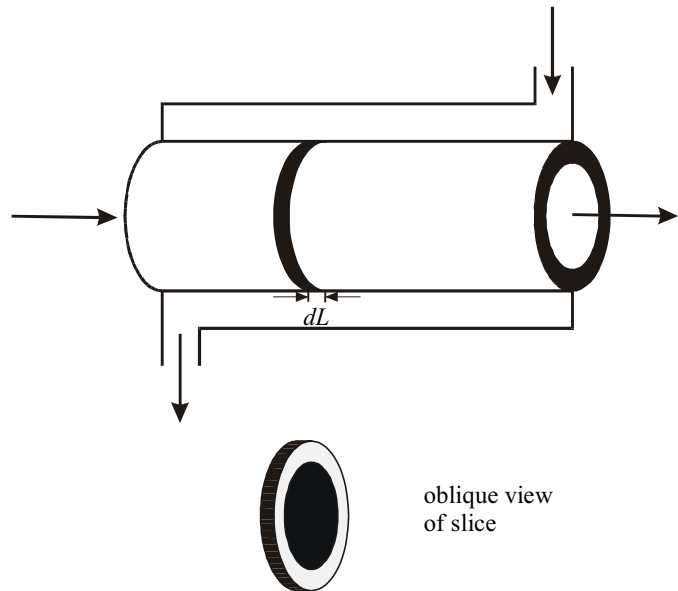
- U and c_p 's are constant
- ΔH of neither stream has contributions from both sensible and latent heats (i.e. ΔH is either all sensible heat or all latent heat)

Actually, we assumed in the analysis above that ΔH was all sensible heat for both streams. In the homework, you will show that ΔH can also be all latent heat and the LMTD is still the appropriate average driving force. For example, if you use condensing steam as your hot fluid, as long as the steam remains saturated:

for saturated steam:

$$T'(x) = \text{const} = T_{bp}$$

We also assumed in the analysis above, that the flow was counter-current. You will also show in the first homework problem that the same design equation applies to co-current flow.

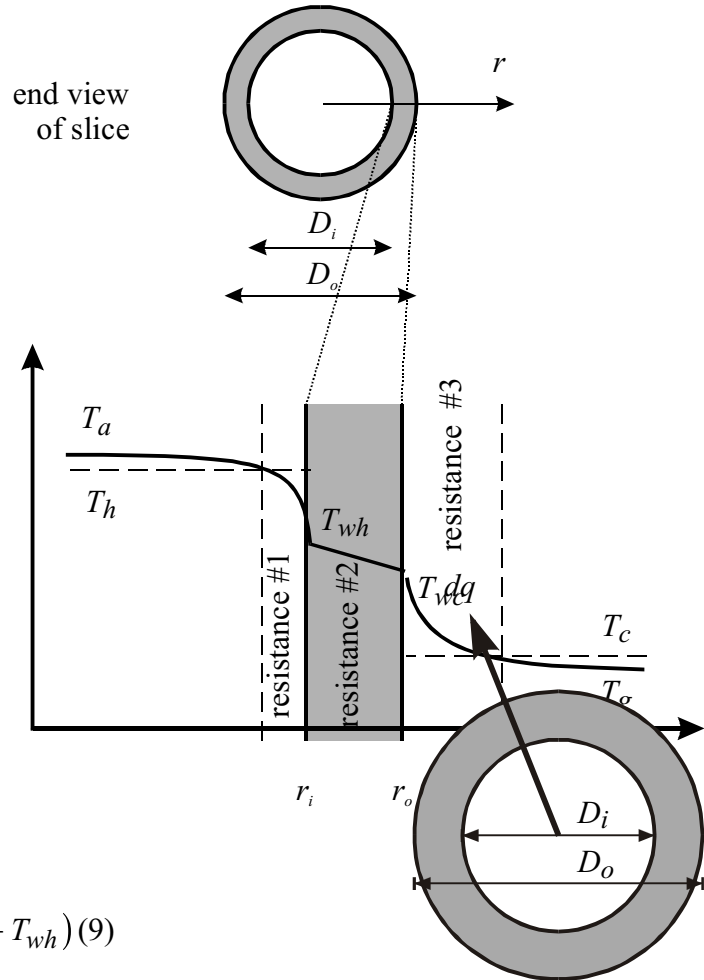


RESISTANCES IN SERIES

Consider heat transfer through the inner pipe of a double-pipe heat exchanger. Let's take a slice out of the heat exchanger and examine the temperature profile along a radius to the pipe at one particular axial position.

One can identify three regions in which the temperature varies sharply. These correspond to the three resistances to heat transfer: the pipe wall itself, the fluid film inside the pipe and the fluid film outside the pipe. These resistances act in series. The total resistance is related to the resistance of each film by:

$$\underbrace{\frac{1}{U_o}}_{\text{total resistance}} = \underbrace{\frac{1}{h_o}}_{\text{resistance of outer film}} + \underbrace{\frac{x_w D_o}{k_w D_L}}_{\text{resistance of pipe wall}} + \underbrace{\frac{1}{h_i} \frac{D_o}{D_i}}_{\text{resistance of inner film}}$$



That resistances add in this way is a very important concept, so I'm going to take the time to prove it to you again. This will also give us an opportunity to review the definitions of the quantities.

Consider the temperature profile along some line drawn perpendicular to the pipe wall through the center of the pipe. These temperature variations drive heat transfer down the temperature hill. The rate dq of heat transferred through some small element of the inner surface of the pipe having area dA_i is

$$dq = h_i \underbrace{dA_i}_{\pi D_i dL} (T_h - T_{wh}) \quad (9)$$

where h_i is a **single-phase heat-transfer coefficient** for the inner film of fluid next to the pipe and dL is the length of the pipe segment. At steady-state, this same rate of heat transfer must occur through the liquid film outside the pipe:

$$dq = h_o \underbrace{dA_o}_{\pi D_o dL} (T_{wc} - T_c) \quad (10)$$

At steady-state, this same rate of heat transfer must also occur through the pipe wall itself:

$$dq = \frac{k_w}{x_w} d\overline{A}_L (T_{wh} - T_{wc}) \quad (11)$$

where k_w is the thermal conductivity of the pipe wall and x_w is the wall thickness. Since the inner and outer areas are somewhat different, we use an average of them in (11):

where

$$d\bar{A}_L = \frac{dA_o - dA_i}{\ln\left(\frac{dA_o}{dA_i}\right)} = \frac{\pi(D_o - D_i)dL}{\ln\left(\frac{D_o}{D_i}\right)} = \pi\bar{D}_L dL$$

is the **log-mean** of dA_o and dA_i . Now we define the **overall heat-transfer coefficient** U_o as

$$dq \equiv U_o dA_o (T_h - T_c) \quad (12)$$

This is called “overall” because we are using the overall driving force in the definition. Solving (12) for the overall temperature difference, then writing this overall as the sum of the individual temperature differences

$$\frac{dq}{U_o dA_o} = T_h - T_c = \underbrace{T_h - T_{hw}}_{\frac{dq}{h_i dA_i}} + \underbrace{T_{hw} - T_{cw}}_{\frac{dq}{\frac{k_w}{x_w} d\bar{A}_L}} + \underbrace{T_{cw} - T_c}_{\frac{dq}{h_o dA_o}}$$

Substituting (9), (10), and (11):

$$\frac{dq}{U_o dA_o} = \frac{dq}{h_i dA_i} + \frac{dq}{\frac{k_w}{x_w} d\bar{A}_L} + \frac{dq}{h_o dA_o}$$

Dividing through by dq/dA_o leaves:

$$\frac{1}{U_o} = \frac{1}{h_i} \frac{D_o}{D_i} + \frac{x_w}{k_w} \frac{D_o}{\bar{D}_L} + \frac{1}{h_o}$$

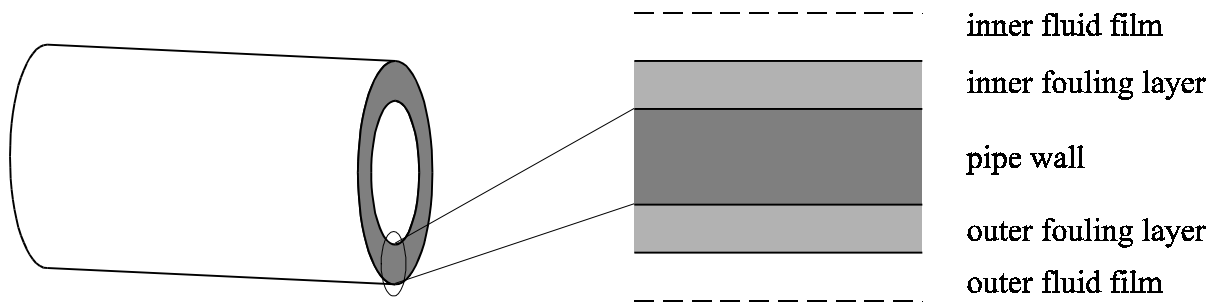
after substituting the expressions relating the dA 's to D 's and dL .

Heat transfer coefficients (either U or h) are like conductances in electricity: the heat flux is proportional to them (like electrical current through a resistor is proportional to its conductance). The reciprocal of the heat transfer coefficients ($1/U$ or $1/h$) is like an electrical resistance. The formula above (relating $1/U$ to $1/h$'s) is like that relating the overall resistance of a circuit composed of three resistors in series: the total resistance is the sum of each of the three individual resistances.

FOULING FACTORS

The usefulness of analogies is that we can extend our knowledge in one area using knowledge in other. For example, if there are additional layers through which heat must be conducted, then we can just add their resistances to get the total. A situation involving additional layers is:

fouling — deposition of dirt, scale or any solid deposit on one or both sides of the tube



Fouling generally reduces heat transfer by imposing an additional resistance. Its effect is accounted for by use of

fouling factors:

$$h_d = \frac{k_d}{x_d}$$

There may be a fouling factor for both the inside and the outside of the pipe. Adding these resistances to the others:

$$\frac{1}{U_o} = \frac{1}{h_o} + \underbrace{\frac{1}{h_{do}}}_{\text{fouling outside pipe}} + \frac{x_w}{k_w} \frac{D_o}{D_L} + \underbrace{\frac{1}{h_{di}} \frac{D_o}{D_i}}_{\text{fouling inside pipe}} + \frac{1}{h_i} \frac{D_o}{D_i}$$

By means of the electrical analogy, we are able to guess the form of the correction without having to go through the analysis.

CORRELATIONS TO ESTIMATE h 'S

In all the problems we have worked so far, we have been given the values of the 1-phase heat transfer coefficients (the h_i and h_o). Now we are going to turn our attention to how these can be estimated if they are not otherwise known. The empirical correlations appropriate for a given situation usually depend on three questions:

1. What is the geometry? (e.g flow inside pipe, flow across bank of tubes, flow around sphere)

2. Is the flow turbulent or laminar?
3. Does a phase change occur?

Our book presents a number of common correlations which cover the most common situations:

Sect. 4.5, 4.6 - without phase change
 laminar flow inside tubes - p238 (not covered in class)
 turbulent flow inside tubes - 239-244 ♣

Sect. 4.8 - with phase change (not covered in class)

For flow inside long tubes, the criteria for turbulent flow is simple: just calculate the **Reynolds number**:

$$N_{\text{Re}} = \frac{\rho \langle v \rangle D_i}{\mu} = \frac{G D_i}{\mu}$$

where

ρ = fluid density

μ = fluid viscosity

$\langle v \rangle$ is the cross-sectional average fluid velocity

The latter quantity is defined as

$$\langle v \rangle = \frac{Q}{S_i}$$

where

Q = volumetric flowrate through tube (units of volume per time)

$S_i = \pi D_i^2 / 4$ = cross-section area of tube

Another term which is sometimes used to calculate Reynolds number is the **mass velocity**:

$$G \equiv \rho \langle v \rangle = \frac{\rho Q}{S_i} = \frac{\dot{m}}{S_i} \quad (\text{units of mass per area per time})$$

The mass velocity is often used in problems involving gas flow where both density and velocity depend on pressure, but their product is independent of pressure (since it represents mass flowrate and at steady state, a mass balance requires the mass flowrate to be the same at all axial positions). However Reynolds number is calculated, the criteria for turbulent flow is as follows:

$N_{\text{Re}} > 6000 \Rightarrow$ flow is turbulent

$N_{\text{Re}} < 2100 \Rightarrow$ flow is laminar

$2100 < N_{\text{Re}} < 6000 \Rightarrow$ flow is in transition

♣ You should make a special effort to read these pages before working the HWK problems, since I don't have time in class to present all the details.

h_i for Turbulent Flow In Long Pipes

For turbulent heat transfer in long pipes, the individual film coefficient inside a pipe can be estimated using the **Sieder-Tate equation** [eq. (4.5-8) in G]: ♦

$$\underbrace{\frac{h_i D_i}{k}}_{N_{Nu}} = 0.023 \underbrace{\left(\frac{\rho \langle v \rangle D_i}{\mu} \right)^{0.8}}_{N_{Re}} \underbrace{\left(\frac{c_p \mu}{k} \right)^{1/3}}_{N_{Pr}} \left(\frac{\mu}{\mu_w} \right)^{0.14}$$

where

$$\begin{aligned} k &= \text{thermal conductivity of fluid inside tube} \\ c_p &= \text{heat capacity (specific heat) of fluid inside tube} \\ \mu &= \text{viscosity of fluid inside tube} \end{aligned}$$

Unless specifically indicated, all fluid properties are evaluated at the mixing-cup temperature of the fluid:

$$\mu, k, c_p \text{ evaluated at } T$$

The subscript “w” indicates the property is to be evaluated at the wall temperature:

$$\mu_w \text{ evaluated at } T_w$$

Experimentally, one finds that heat transfer coefficients can be different for heating and cooling over the same temperature range. The reason, is that the viscosity at the wall is very important in determining transport and μ_w can be very different from μ . This is accounted for in the μ/μ_w factor.

Which *T* do you use for property evaluations?

When the inlet and outlet *T*'s differ, what *T* do you use to evaluate the properties at? Use arithmetic mean values for *T* and *T_w*:

$$\bar{T} = \frac{T_a + T_b}{2} \quad \text{and} \quad \bar{T}_w = \frac{T_{wa} + T_{wb}}{2}$$

where the subscript “a” refers to the inlet and “b” refers to the outlet. Since the outlet *T* and the outlet *T_w* depend on the heat transfer coefficient, this makes the determination of *h* a trial-and-error (see Example 4.5-2).

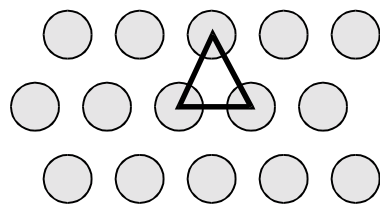
♦ The coefficient of 0.023 in this equation is the value which appears in McCabe, Smith & Harriott. Geankoplis gives a value of 0.027 instead. In homeworks and exam, you can use either value. The Notes use 0.023 because most of the homework problems using this equation were taken from MS&H.

Chapter 4. Shell-and-Tube Heat Exchangers

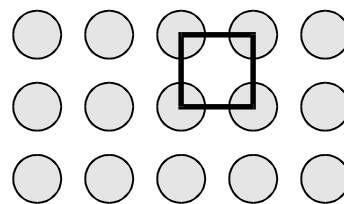
The value of h_o for shell-and-tube heat exchangers depends on arrangement of tubes and baffles inside the shell. We will first describe typical arrangements and then give a common correlation for h_o .

TUBE PITCH

The bundle of tubes in a shell-and-tube heat exchanger can be stacked in one of two different ways



triangular pitch
(advantage: closer packing)

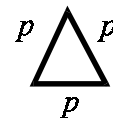


square pitch
(advantage: easier cleaning)

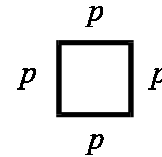
The use of triangular pitch allows the tubes to be more tightly packed -- more tubes and therefore more area per unit volume of shell. This makes the shell cheaper.

On the other hand, the square pitch has the advantage that it is easier to clean. You can get a long brush in between two rows or between two columns. Of course, the shell has to be pulled off of the tube bundle before you can get at it in either case.

Regardless of which geometry is used, the center-to-center distances between adjacent tubes is called the *tube pitch*.



$$p \geq \frac{5}{4} D_o$$



$$p \geq D_o + \frac{1}{4} \text{ inch}$$

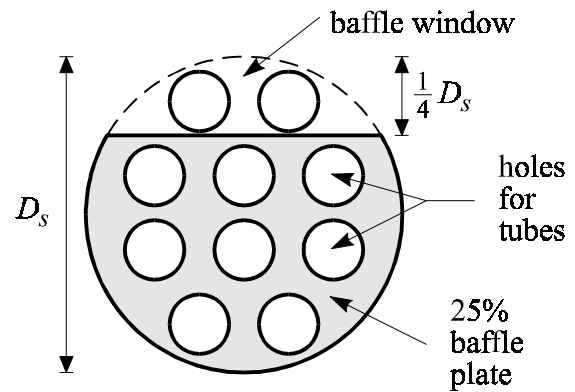
BAFFLES

To some extent, it is advantageous to reduce the cross-sectional area available for flow. For the same volumetric flowrate, this will increase the mass flux or the mass velocity of the fluid flow, which will increase h_o . Of course, this also increases the pressure drop and the pumping cost.

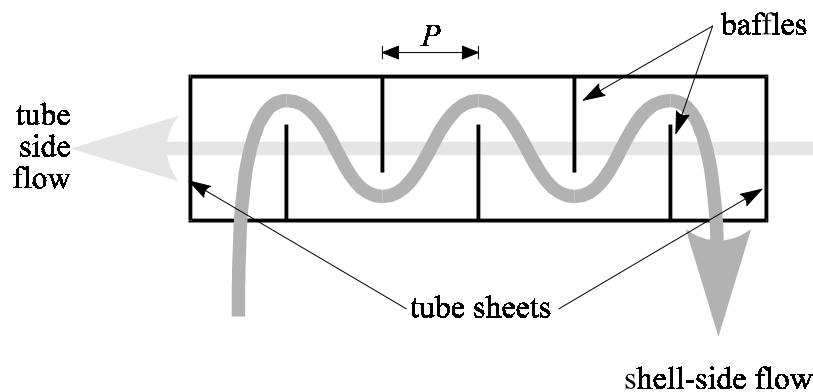
A common technique for thus increasing h_o is to install baffle plates, which partially block the cross-sectional area on the shell side. A baffle plate is a disk whose diameter is the inside diameter of the shell:

$$D_s = \text{diameter of shell}$$

with holes drilled through it for the tubes to pass through. Part of the disk is cut off to form what is called the **baffle window**, which is the cross section available to the shell-side of the fluid. When the height of the window is $1/4$ of the shell diameter, we call the plate a **25% baffle**.



A number of these plates is placed along the length of the exchanger with the location of the baffle window alternating between the top and bottom of the plate.



A second advantage of these plates is that they prevent the formation of large stagnant regions (having low heat transfer rates) which usually accompany “channelling” of the fluid in a direction path connecting inlet to outlet. The spacing between the baffle plates is called the **baffle pitch**:

$$P = \text{baffle pitch}$$

Typical baffle pitch is a fraction of the shell diameter:

$$0.2 < P/D_s < 1$$

Besides reducing the area available for flow on the shell side, the baffles also force the fluid across all of the tubes, which normally will enhance the heat transfer coefficient.

h_o FOR SHELL-AND-TUBE EXCHANGER

Reference: McCabe, Smith & Harriott, 5th ed., p432-436

An approximate but generally useful correlation for estimating the shell-side coefficient in a shell-and-tube heat exchanger is the **Donohue equation**:

$$\frac{h_o D_o}{k} = 0.2 \left(\frac{D_o G_e}{\mu} \right)^{0.6} \left(\frac{c_p \mu}{k} \right)^{0.33} \left(\frac{\mu}{\mu_w} \right)^{0.14} \quad (13)$$

where μ , k and c_p are properties of the shell-side fluid. The form of this equation is very similar to the Sieder-Tate equation, except the exponents and coefficient are different. Another difference is that the mass velocity G_e is a weighted average

$$G_e = \sqrt{G_b G_c} \quad (\text{geometric mean})$$

of the mass velocity through the baffle window

$$G_b = \frac{\dot{m}}{S_b}$$

and the mass velocity for crossflow perpendicular to the tubes

$$G_c = \frac{\dot{m}}{S_c}$$

where S_b is the area available for flow of the shell-side fluid through the baffle window and S_c is the interstitial area available for crossflow perpendicular to the bank of tubes at the widest point in the shell.

$$\underbrace{S_b}_{\text{area of blue region}} = f_b \left(\frac{\pi D_s^2}{4} \right) - N_b \left(\frac{\pi D_o^2}{4} \right) \quad (14)$$

where D_s = diameter of entire shell

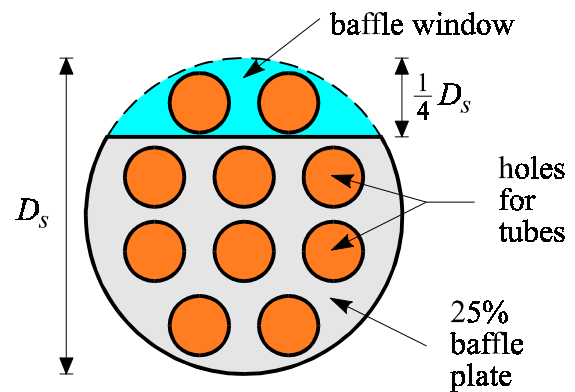
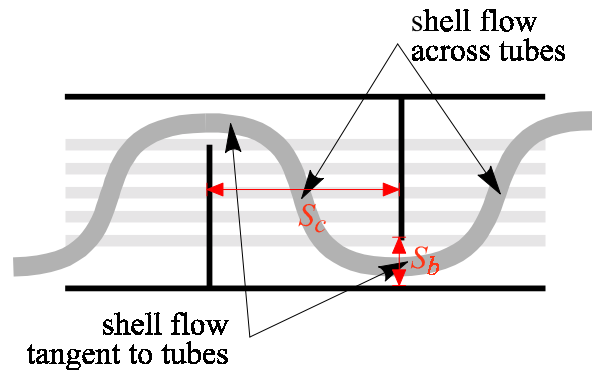
N_b = number of tubes in baffle window

f_b = area fraction of baffle plate that is window

For a 25% baffle plate, we have

$$f_b = 0.1955 \quad (15)$$

The second area is calculated from

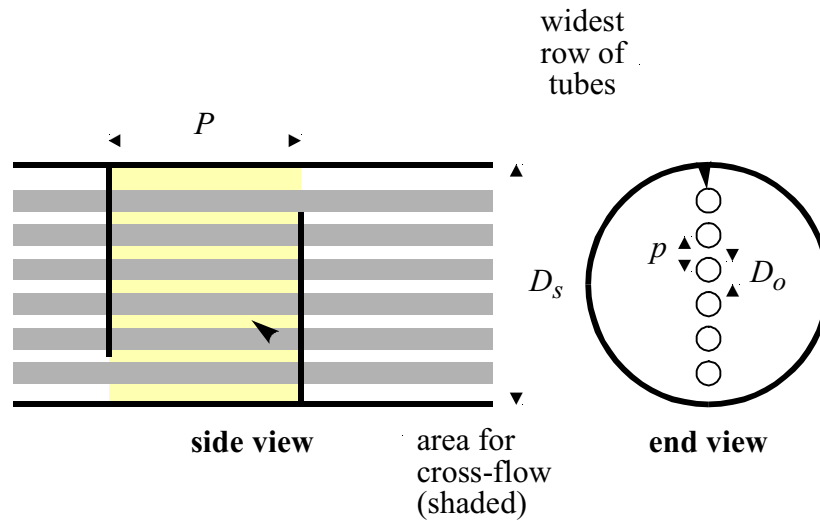


$$S_c = PD_s \left(1 - \frac{D_o}{p} \right)$$

p = tube pitch
 P = baffle pitch

Appendix: Derivation for S_b and S_c

In case you are curious as to how these formulas we obtained, I have put their derivation in this appendix.



S_c is the area open to fluid flow across the widest row of tubes in the shell and between two adjacent baffle plates. First the total area (ignoring tubes) is

$$\text{total area} = PD_s$$

where P is the baffle pitch. To calculate the fraction of PD_s which is open, let's subdivide D_s into repeating unit cells:

$$\text{length of unit cell} = p \text{ (tube pitch)}$$

$$\text{length which is open} = p - D_o$$

$$\text{fraction open} = (p - D_o)/p = 1 - D_o/p$$

Multiplying this fraction by the total area gives the area open:

$$S_c = PD_s \left(1 - \frac{D_o}{p} \right) \quad (16)$$

Of course, we have ignored some end effects which could be significant if the number of tubes is not large.

Likewise the open area of a baffle window is the total area of the window minus the area blocked off by tubes:

$$S_b = f_b \left(\frac{\pi D_s^2}{4} \right) - N_b \left(\frac{\pi D_o^2}{4} \right)$$

where $f_b = 0.1955$ (for a 25% baffle)

and $N_b =$ no. of tubes thru window

To get this value of f_b , we have to do a little geometry. First, recall that the area of a circle of radius r is πr^2 .

$$A_{circle} = \pi r^2$$

A “sector” is a portion of a circle (see figure at right):

$$A_{sector} = \frac{1}{2} r^2 \underbrace{(\theta)}_{\substack{\text{total angle} \\ \text{subtended} \\ \text{by sector}}}$$

where θ is the total angle subtended by the arc of the sector. Note that if we substitute 2π for the θ , we get the $A_{sector} = A_{circle}$. The area of the triangle whose sides are x , y , and r equals

$$A_{triangle} = \frac{1}{2} bh = \frac{1}{2} xy$$

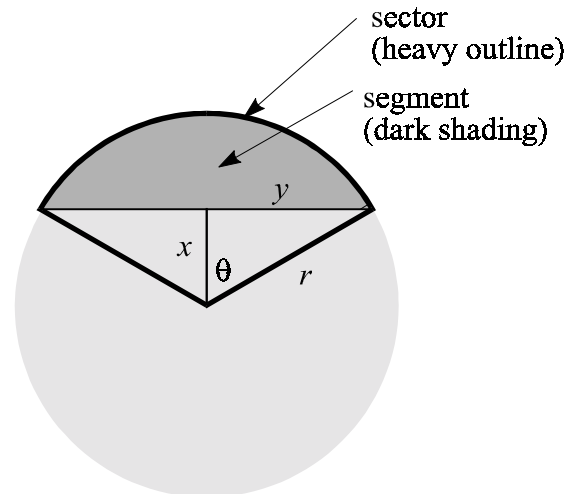
Finally, the area of the segment is calculated from

$$A_{segment} = A_{sector} - 2A_{triangle}$$

For a 25% baffle, the height of the segment, $r-x$, will be 25% of the diameter -- or 50% of the radius:

$$\frac{x}{r} = 0.5 \Rightarrow \theta = \cos^{-1}(0.5) = 60^\circ = \frac{\pi}{3} \Rightarrow y = \sqrt{r^2 - x^2} = \frac{\sqrt{3}}{2} r$$

$$A_{triangle} = \frac{1}{2} \left(\frac{r}{2} \right) \left(\frac{\sqrt{3}}{2} r \right) = \frac{\sqrt{3}}{8} r^2 = 0.217 r^2$$



$$A_{\text{sector}} = \theta r^2 = \frac{\pi}{3} r^2$$

$$A_{\text{segment}} = \frac{\pi}{3} r^2 - 2 \left(\frac{\sqrt{3}}{8} r^2 \right) = \left(\frac{\pi}{3} - \frac{\sqrt{3}}{4} \right) r^2 = 0.61418 r^2$$

Now f_b is the fraction of the total area of the circle which is represented by this segment:

$$f_b = \frac{A_{\text{segment}}}{A_{\text{circle}}} = \frac{\left(\frac{\pi}{3} - \frac{\sqrt{3}}{4} \right) r^2}{\pi r^2} = \frac{0.61418}{3.1416} = 0.1955$$

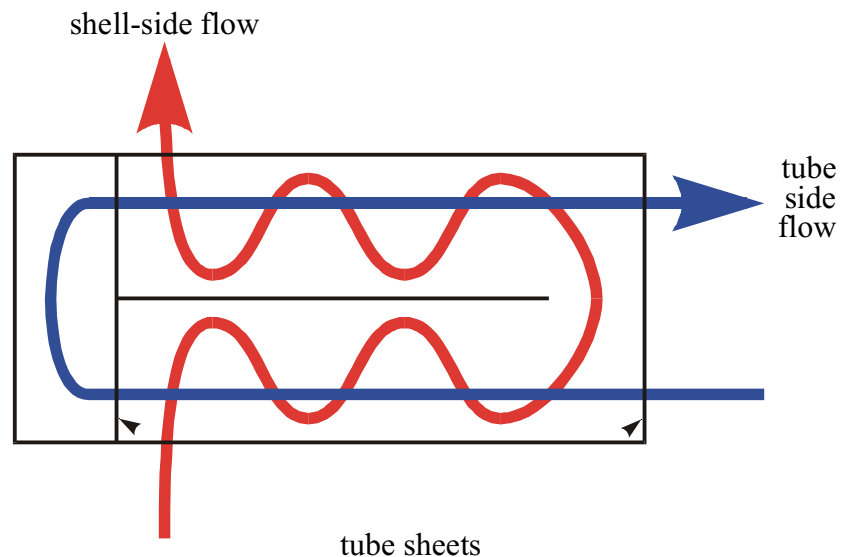
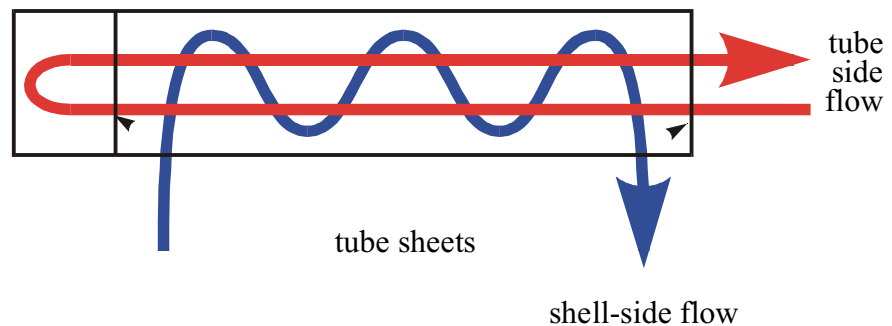
MULTIPASS CONSTRUCTION

Just as we can improve the heat transfer coefficient on the shell side by reducing the baffle pitch, we can improve the heat transfer coefficient on the tube side by restricting the flow to half of the tubes. Both have the effect of reducing the area available for flow, thereby increasing the fluid velocity and the heat transfer coefficient.

Suppose we partition the manifold in such a way that the inlet fluid can only enter half of the tubes. The other half of the tubes are used for return flow. We say that such an exchanger has **two tube passes**.

Although two tube passes improves h_i , one of the passes will be co-current. A 2-4 exchanger improves both h_i and h_o , and in addition, the flow is more nearly countercurrent. We could also partition the shell side with a horizontal baffle in addition to the vertical baffles, producing **two shell passes**.

The most commonly used designs are:



- 1-2 exchanger
- 2-4 exchanger

where the first number is the number of shell passes and the second number is the number of tube passes.

An even number of tube passes is desirable because then input and output of the tube-side fluid occur on the same end of the exchanger. This allows the other end of the exchanger to "float" in response to thermal expansion of the metal, which can otherwise be a serious problem when the shell changes temperature during startup or shutdown.

"TRUE" MEAN TEMPERATURE DIFFERENCE

For multipass construction, the flow is neither counter-current nor co-current. As a consequence, the *average* driving force is no longer the LMTD. As it turns out, what is called the *true mean temperature difference* (MTD) is somewhat less than the log-mean:

$$\Delta T_m = F_T \Delta T_L \quad (17)$$

This is the ΔT , which when multiplied by UA gives the total rate of heat transfer for a shell-and-tube exchanger:

$$q_T = U_o A_o \Delta T_m$$

F_T is a correction factor which is unity for pure co-current or pure counter-current flow:

$$F_T = 1$$

For pure crossflow to a bank of tubes, or for a mixture of crossflow and counter-current flow, the factor is less than unity:

$$F_T = F_T(Y, Z, \text{type of flow}) \leq 1$$

where Y and Z are ratios of temperature differences:

$$Y = \frac{T_{cb} - T_{ca}}{T_{ha} - T_{cb}} \quad \text{and} \quad Z = \frac{T_{ha} - T_{hb}}{T_{cb} - T_{ca}}$$

where the subscript "c" refers to the cold fluid while the subscript "h" refers to the hot fluid and the subscript "a" refers to the inlet while "b" refers to the outlet.

F_T is usually plotted as a function of Y for different values of Z . Such a plot is sketched at right. More accurate plots can be found in Geankoplis's book:

1-2 HX \rightarrow Fig. 4.9-4a

2-4 HX \rightarrow Fig. 4.9-4b

Note that as $Z \rightarrow 0$, $F_T \rightarrow 1$ over the entire range of $Y < 1$. This special case is applicable for condensing vapors. As long as the vapor is condensing, its temperature stays at the boiling point:

$$T_{ha} = T_{hb} = T_{bp}$$

so that

$$Z = 0 \text{ and } F_T = 1$$

for condensing steam as the hot fluid. Similarly if we have boiling water as the "cold" fluid, its temperature doesn't change (i.e. $T_{ca} = T_{cb} = T_{bp}$) and then we have

$$Y = 0 \text{ and } F_T = 1$$

Although the flow in the exchanger is complex, we calculate $\overline{\Delta T}_L$ in (17) as if the flow were counter-current. The deviation caused by not being counter-current is included in the values of the empirical correction factor F_T .

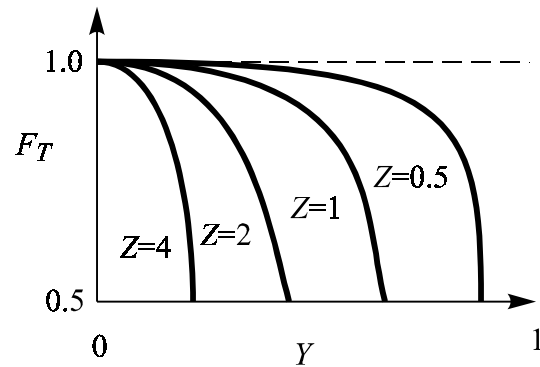
Example: A steel mill is considering whether a spare heat-exchanger will be able to cool of 3000 gal/hr of a dilute acid from 250°F to 180°F using 5000 gal/hr of 80°F river water. You are asked to estimate: a) the true-mean driving force, ΔT_m , and b) the shell-side coefficient, h_o .

Description of available heat exchanger:

- type: 1-2
- tubes: 158 1-inch, 14BWG stainless tubes, 16 ft long, stacked in 1¼ inch square pitch
- baffles: 25% with 6 inch pitch
- shell: 20 inch inside diameter, mild steel

Solution: First we have to determine the outlet temperature of the cold stream. The rate of energy lost by the hot stream is the rate of energy gained by the cold stream

$$q_T = \dot{m}_h c_{ph} (T_{ha} - T_{hb}) = \dot{m}_c c_{pc} (T_{cb} - T_{ca})$$



Assuming the physical properties of dilute acid and river water are the same as pure water, we can take $c_{ph} = c_{pc}$ so that heat capacity can be cancelled out of the second equation above, leaving

$$\frac{T_{cb} - T_{ca}}{T_{ha} - T_{hb}} = \frac{\dot{m}_h c_{ph}}{\dot{m}_c c_{pc}} \approx \frac{\dot{m}_h}{\dot{m}_c} = \frac{3000 \text{ gal/hr}}{5000 \text{ gal/hr}} = 0.6 \quad (18)$$

From the problem statement we have

$$T_{ha} = 250^\circ\text{F} \quad T_{hb} = 180^\circ\text{F} \quad T_{ca} = 80^\circ\text{F}$$

Substituting these into (18) and solving for T_{cb} , we obtain

$$T_{cb} = 122^\circ\text{F} \blacklozenge$$

Next, we calculate the two quantities needed to evaluate the true-mean driving force:

$$Z = \frac{T_{ha} - T_{hb}}{T_{cb} - T_{ca}} = \frac{1}{0.6} = 1.67 \quad \text{and} \quad Y = \frac{T_{cb} - T_{ca}}{T_{ha} - T_{ca}} = 0.247$$

Since this is a 1-2 exchanger, we read F_T from Fig. Fig. 4.9-4a:

$$F_T = 0.97$$

Although the flow in the exchanger is complex, we calculate $\overline{\Delta T}_L$ as if the flow were counter-current:

$$\Delta T_1 = T_{ha} - T_{cb} = 128^\circ\text{F} \quad \text{and} \quad \Delta T_2 = T_{hb} - T_{ca} = 100^\circ\text{F}$$

$$\overline{\Delta T}_L = \frac{\Delta T_1 - \Delta T_2}{\ln \frac{\Delta T_1}{\Delta T_2}} = 113^\circ\text{F}$$

Finally

$$\Delta T_m = F_T \overline{\Delta T}_L = 110^\circ\text{F}$$

The shell-side coefficient (h_o) can be estimated using Donohue's correlation (13). Since acid is corrosive, we would be well-advised to place it inside the stainless tubes, leaving river water on the shell side (which is mild steel). With this choice, the mass flowrate is

◆ Such a high temperature in the river could be harmful to fish and other wildlife. Engineers need to be mindful of the impact of their designs on the environment as well as on the health and safety of people in the vicinity. Faced with this result, the engineer should suggest altering the design (e.g. increase the flowrate of cooling water to obtain a lower increase in temperature). For the purpose of this academic example, we will ignore this objection and proceed through the analysis.

$$\dot{m} = \left(5000 \frac{\text{gal}}{\text{hr}} \right) \left(8.34 \frac{\text{lb}}{\text{gal}} \right) = 4.17 \times 10^4 \frac{\text{lb}}{\text{hr}}$$

For crossflow, the maximum available area for flow can be calculated from (16):

$$S_c = PD_s \left(1 - \frac{D_o}{p} \right) = 0.167 \text{ ft}^2$$

using $P = 6$ inch, $D_s = 20$ inch, $D_o = 1$ inch (see Appendix A.5-2), and $p = 1.25$ inch. The mass velocity for cross-flow is

$$G_c = \frac{\dot{m}}{S_c} = 2.5 \times 10^5 \frac{\text{lb}}{\text{ft}^2 \cdot \text{hr}}$$

Let's assume that the fraction of tubes which pass through the baffle window equals the fraction of the shell cross-section represented by the baffle window. In other words:

$$N_b = f_b \times 158 = 0.1955 \times 158 = 30.8$$

where 158 was given as the total number of tubes in the shell and $f_b = 0.1955$ applies for 25% baffle windows (see (15) and Appendix on page 20). Now everything in (14) is known:

$$S_b = f_b \left(\frac{\pi D_s^2}{4} \right) - N_b \left(\frac{\pi D_o^2}{4} \right) = 0.258 \text{ ft}^2$$

The mass velocity through the baffle window is

$$G_b = \frac{\dot{m}}{S_b} = 1.62 \times 10^5 \frac{\text{lb}}{\text{ft}^2 \cdot \text{hr}}$$

and the effective mass velocity is

$$G_e = \sqrt{G_b G_c} = 2.01 \times 10^5 \frac{\text{lb}}{\text{ft}^2 \cdot \text{hr}}$$

Before we can estimate h_o from (13), we need some fluid properties. Since we have no idea what the wall temperature is, let's just get a rough estimate of h_o by setting $\mu/\mu_w = 1$. The other properties (besides μ_w) are evaluated at the average temperature of the shell-side fluid [$T = 0.5(80^\circ\text{F} + 122^\circ\text{F}) = 101^\circ\text{F}$ (38.3°C)]. Using Appendix A.2:

$$\mu = 0.681 \text{ cP}, \quad k = 0.363 \text{ BTU/ft}\cdot\text{hr}\cdot^\circ\text{F}, \quad \rho = 62.0 \text{ lb/ft}^3, \quad c_p = 0.999 \text{ BTU/lb}\cdot^\circ\text{F}$$

(13) yields

$$h_o = 363 \text{ BTU/ft}^2\cdot\text{hr}\cdot^\circ\text{F}$$

Once we have h_o and h_i we can estimate T_w and iterate until the area required no longer changes.

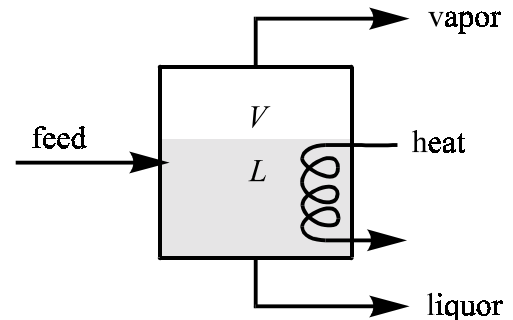
Chapter 5. Evaporation

evaporation -- concentrating a solution containing a nonvolatile solute by boiling away the solvent (usually water)

Examples:

- production of orange juice concentrate
- production of concentrated H_2SO_4
- production of distilled water

Usually the product is a concentrated solution (called the “liquor”) and the vapor is condensed and discarded.



liquor - the concentrated solution

An important exception is the production of **distilled water** from tap water. Here the condensed vapor is the product and the more concentrated solution of minerals or (in the case of **desalination**) salts is discarded.

Evaporation is not the only unit operation that involves boiling. Some others that involve boiling include:

- distillation - involves two or more volatile components (evaporation has just one)
- drying - product is a solid (in evaporation, product is usually a more concentrated liquid solution)
- crystallization - product is a slurry of crystals precipitated from solution (not a simple solution)

Usually these differences are sufficient to require different equipment to perform the operation.

EQUIPMENT FOR EVAPORATION

There are several types of evaporators, but they all have the following parts:

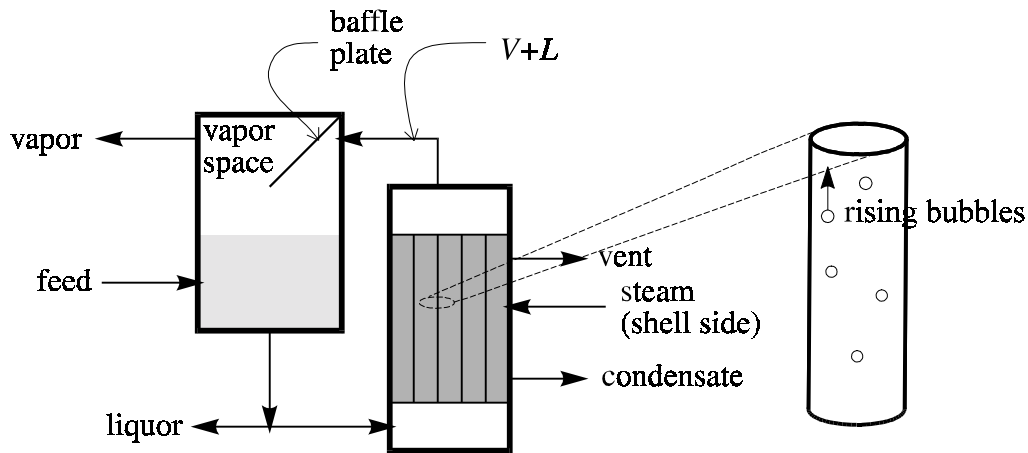
Part #1: HX (for adding the latent heat of vaporization to the liquid feed). Usually HX is a shell-and-tube with condensing steam as the hot fluid on the shell side (because steam is free of minerals which form scale).

Part #2: vapor space or vapor head (larger chamber in which liquid, entrained in the vapor as droplets or foam, can be separated from the vapor, usually by impinging stream onto a plate.)

You also need something to move the liquid through the heat exchanger. Sometimes a pump is used and sometimes it's just left to gravity, either in the form of a falling film on the outside of the HX tubes or the entrainment of liquid by rising bubbles.

Part #3: liquid mover

- pump
- gravity - falling film



- gravity - entrainment by rising bubbles

Long-Tube Vertical Evaporator

When the heat exchanger tubes are oriented vertically, the bubbles produced by boiling rise and carry liquid with them. Tubes are typically 1 or 2 inches in diameter and 12 to 32 feet in length. The liquid entrained in the vapor coming out of the HX is richer in solute than that entering the HX. Vapor and fine liquid droplets are separated in the vapor head by placing a ***baffle plate*** in the path of the two-phase fluid coming out of the HXer.

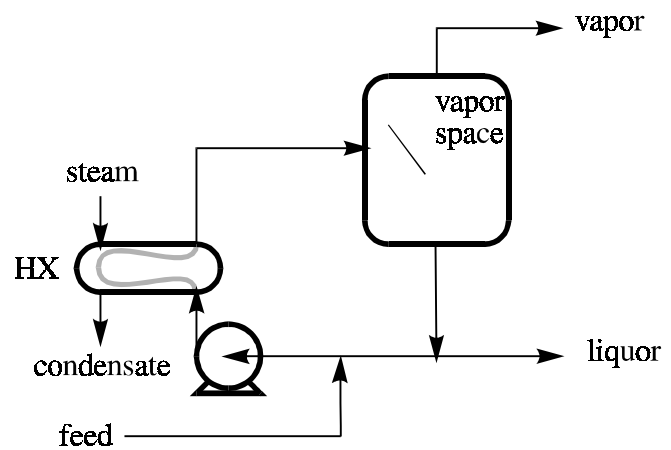
Notice the ***vent*** at the top of the shell-side of the HX. Usually a very small fraction of the steam flow is allowed to bleed out of the shell. This is done to allow air which is often mixed with the steam to escape. Otherwise non-condensable gases will accumulate in the shell, causing the pressure to rise and decreasing the steam flowrate.

Long-tube vertical evaporators are especially effective in concentrating liquids that tend to foam. Foam is broken when the two-phase mixture hits the baffle plate.

Forced-Circulation Evaporator

Many concentrated solutions are highly viscous. For example, a concentrated sugar solution can have a viscosity that is 10^6 times larger than water. If the concentrated solution is highly viscous, the velocity of rising bubbles will be very small and the heat transfer coefficient will also suffer.

For very viscous liquids, a pump is often used to improve the circulation. Of course a pump also raises the pressure significantly which can prevent the liquid from boiling. In a forced-circulation evaporator, boiling usually occurs near the end of the HX where the pressure is lower or in the pipe leading from the HX to the vapor space.



HX tubes are now oriented horizontally so they are easier to clean. Again a baffle plate is used to separate vapor from entrained liquid.

EVAPORATOR PERFORMANCE

Regardless of which type of evaporator we use, there are two standard measures of performance:

capacity – pounds water evaporated per hour

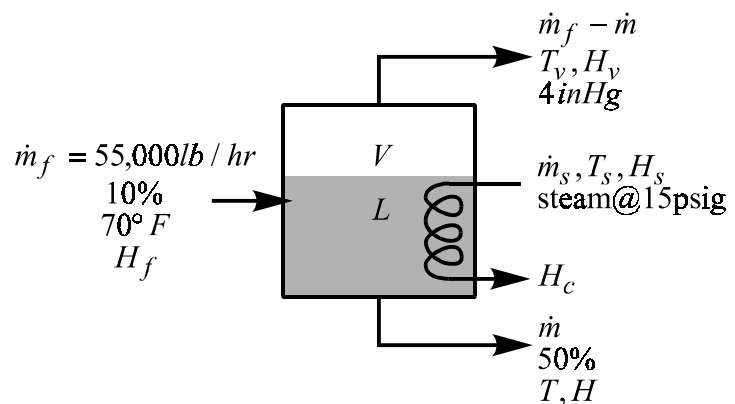
economy – lb water evaporated per lb steam used (usually somewhat less than unity)

EXAMPLE: SIMPLE EVAPORATOR PROBLEM

Suppose we are trying to concentrate a solution of orange juice from 10wt% solids to 50wt% in a long-tube vertical evaporator. Our past experience has shown that a reasonable heat transfer coef. is

Given: $U = 500 \text{ Btu/h-ft}^2\text{-}^\circ\text{F}$

To keep the boiling T low enough, we keep the vapor space under vacuum:



$$p = 4 \text{ inHg}$$

If the feed is 55,000 lb/hr at 70°F, what area of heat exchanger is required and what flowrate of 15 psig steam?

Find: \dot{m}_s, A

First we do a mass balance to determine the flowrates. A mass balance on the solids yields:

$$10\%(55,000 \text{ lb/hr}) = 50\%(\dot{m})$$

so $\dot{m} = 11,000 \text{ lb/hr (liquor)}$

is the flowrate of the liquor. The corresponding flowrate of the vapor must be (from an total mass balance):

$$\dot{m}_f - \dot{m} = 44,000 \text{ lb/hr (vapor)}$$

The heat duty of the HXer is just the heat gained by the feed. In terms of enthalpies of the streams:

$$q = \text{vapor} + \text{liquor} - \text{feed}$$

$$q = (\dot{m}_f - \dot{m})H_v + \dot{m}H - \dot{m}_fH_f \quad (19)$$

For high-molecular-weight substances like orange juice and other “organic colloids”[♥] we can neglect **boiling-point elevation** and **heat of dilution**. Then the enthalpies of the feed and the liquor are essentially the properties of pure water under those conditions. The enthalpy of liquid water and water vapor can be read from the Steam Tables found in Appendices A.2-9 and A.2-10 (pages 857-861).[♦]

[♥] “Organic colloids” are solutions of high molecular-weight polymers or dispersions of fine particles. Then the molar concentration of these solutions is negligibly small and their properties are close to that of pure water: see example on page 35. An example of an organic colloid is orange juice.

[♦] For consistency with later examples in which heat of dilution effects are important, we read all the enthalpies from the steam tables, which have a reference state (where H is defined to be zero btu/lb) corresponding to saturated liquid water at its freezing point. In Example 8.4-1 on p498, Geankoplis works a very similar problem in which all enthalpies are calculated using the conditions of the liquor as the reference state. Then (by definition) H in (19) is zero; the enthalpy of the feed H_f differs from that of the liquor just in sensible heat, which can be estimated as (8.4-9); and the enthalpy of the vapor H_v differs from that of the liquor just in latent heat (i.e. H_v is just the heat of vaporization at the T,p of the vapor space). See the discussion on “steam economy” on page 33. Try re-working Example 8.4-1 evaluating the enthalpies appearing in (8.4-7) using the steam tables (as above): you should get very nearly the same answer.

at 70 °F:♠

$$H_f = 38.09 \text{ btu/lb}_m$$

But what is the temperature of the liquor? Well, since the liquor is in equilibrium with the vapor, their temperature and pressure should be the same. Since the vapor is just saturated steam at 4 inHg, we look up its properties in the steam table:

$$p_v = 4 \text{ inHg} = 1.97 \text{ psia}$$

from App. A.2-9 (p858):

$$T = 125.1 \text{ °F}$$

Interpolating the tables,♣ we obtain

at 125.1 °F: $H_v = 1115.7 \text{ btu/lb}_m$ and $H = 93.1 \text{ btu/lb}_m$

Substituting back into (19):

$$\begin{aligned} q &= \left(44,000 \frac{\text{lb}}{\text{hr}}\right) \left(1115.7 \frac{\text{btu}}{\text{lb}}\right) + \left(11,000 \frac{\text{lb}}{\text{hr}}\right) \left(93.1 \frac{\text{btu}}{\text{lb}}\right) - \left(55,000 \frac{\text{lb}}{\text{hr}}\right) \left(38.09 \frac{\text{btu}}{\text{lb}}\right) \\ &= 4.91 \times 10^7 + 0.10 \times 10^7 - 0.21 \times 10^7 = 4.80 \times 10^7 \frac{\text{btu}}{\text{hr}} \end{aligned}$$

Now, using the design equation, we can calculate the required area:

$$q = UA\Delta T_m \quad (20)$$

In a typical evaporator problem, steam is condensing on the shell side while water is evaporating on the tube side. When a phase change occurs with a single component (water in this case), the temperature stays at the boiling point. Thus the driving force ΔT is practically constant along the length of the heat exchanger.

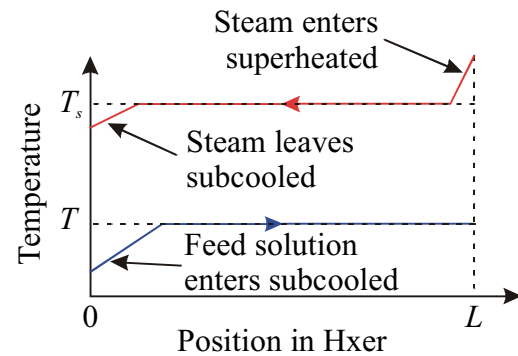
♠ Strictly speaking, the enthalpies tabulated in A.2-9 are for saturated liquid, meaning that the pressure on the liquid equals the vapor pressure. Here the pressure on the feed is probably 1 atm (or 14.7 psia) rather than 0.3622 psia (the vapor pressure). Pressure has a very weak effect on the enthalpy of liquid water and the effect of pressure usually neglected. For example, the effect of a change on pressure equal to 1atm on the enthalpy of liquid water can be estimated as

$$\Delta H_T = \Delta p V \approx (1 \text{ atm}) \left(1 \frac{\text{cm}^3}{\text{g}}\right) = 0.044 \frac{\text{btu}}{\text{lb}_m}$$

which is equivalent to a change in temperature of only 0.044 °F. As long as we are dealing with much larger sensible temperature changes, we can neglect the effect of pressure on the enthalpy of liquid water.

♣ In working the homework assignments, you will have frequent need to perform this interpolation. A Mathcad document has been prepared to assist you: <http://www.andrew.cmu.edu/course/06-202/Steamtab.mcd> This file reads the steam table from <http://www.andrew.cmu.edu/course/06-202/STEAMTAB.PRN>. Links to both files can be found at our homepage.

However, some changes might still occur at either end of the heat exchanger. For example, steam might enter superheated, meaning that its temperature is above the boiling point. Until the temperature drops to the boiling point, condensation does not occur. Similarly, so much heat might be removed from the steam, that it completely condenses and is then subcooled below the boiling point. Finally, the feed solution has to be heated up to its boiling point before evaporation occurs.♥ The temperature profile at right illustrates the most general situation.



For a *preliminary design* (which is all we will do in this course), it is customary to approximate the “true mean” MDT as:

$$\Delta T_m \approx T_s - T$$

where

$$T_s = T \text{ of sat'd steam at } p \text{ in steam chest}$$

$$T = T_{bp} \text{ of conc'd liquor at } p \text{ in vapor space}$$

Knowing the pressure of the steam, we can find its temperature in the steam tables:

at 15 psig = 29.7 psia:

$$T_s = 250^\circ\text{F}$$

The heat of vaporization λ_s is the difference between the enthalpy of saturated vapor H_s and the enthalpy of the condensate H_c leaving (assumed here to be saturated liquid):

$$\lambda_s = H_s - H_c = 1164.2 \text{ btu/lb} - 218.6 \text{ btu/lb} = 945.6 \text{ btu/lb}$$

The driving force for heat transfer is the difference in temperature of saturated steam and saturated vapor:

$$\Delta T_m \approx T_s - T = 250 - 125 = 125^\circ\text{F}$$

Now everything in (20) is known except for A :

$$4.77 \times 10^7 \frac{\text{Btu}}{\text{h}} = \left(500 \frac{\text{Btu}}{\text{h} - \text{ft}^2 - ^\circ\text{F}} \right) (A) (125^\circ\text{F})$$

♥ The heat required to preheat the feed from 70°F (the feed conditions) to 125°F (the boiling point at the pressure in the vapor space) is

$$\left(55000 \frac{\text{lb}}{\text{hr}} \right) \left(93.1 \frac{\text{btu}}{\text{lb}} - 38.09 \frac{\text{btu}}{\text{lb}} \right) = 0.30 \times 10^7 \frac{\text{btu}}{\text{hr}}$$

This is only 6.3% of the heat duty q . We are willing to tolerate this size of error in our preliminary design.

or

$$A = 768 \text{ ft}^2$$

The amount of steam required is just the heat duty divided by the latent heat of the steam:

$$\dot{m}_s = \frac{q}{\lambda_s} = \frac{4.80 \times 10^7 \frac{\text{Btu}}{\text{h}}}{945.6 \frac{\text{Btu}}{\text{lb}}} = 50,800 \frac{\text{lb}}{\text{hr}}$$

Recall that our two main performance indicators were “capacity” and “economy”. Capacity is just the rate of evaporation, which will be the flowrate of the vapor. For this example,

$$\text{capacity} = \dot{m}_f - \dot{m} = 44,000 \frac{\text{lb}}{\text{hr}}$$

The economy is the mass of vapor produced per mass of steam consumed:

$$\text{economy} = \frac{\dot{m}_f - \dot{m}}{\dot{m}_s} = \frac{44,000 \frac{\text{lb}}{\text{hr}}}{50,800 \frac{\text{lb}}{\text{hr}}} = 0.87$$

Steam Economy

Why is the economy less than one? The answer becomes clear, if (instead of looking up the enthalpies of water and its vapor in a table) we estimate them as sensible and latent heat. First, let's select the liquor as the reference state for the calculations of the enthalpies. Then

choose liquor as reference: $H = 0$

The vapor is at the same temperature as the liquor so there are not sensible heat changes, but the vapor has a much higher enthalpy owing to its heat of vaporization:

$$H_v = \lambda$$

Since the feed is also a liquid (like the liquor), its enthalpy differs from the liquor only in sensible heat:

$$H_f = c_p(T_f - T)$$

Substituting these enthalpies in (21):

$$(\dot{m}_f - \dot{m})\lambda - \dot{m}_f c_p (T_f - T) = \dot{m}_s \lambda_s$$

or

$$\frac{\dot{m}_f - \dot{m}}{\dot{m}_s} = \underbrace{\frac{\lambda_s}{\lambda}}_{<1} - \frac{\dot{m}_f}{\dot{m}_s} c_p (T - T_f)$$

Generally the heat of vaporization of water decreases with increases in temperature. Since the steam must be hotter than the water being boiled, this means that $\lambda_s < \lambda$. So the first term in the equation for economy is already less than one. The second term decreases it further; this term represents the energy required to preheat the feed up to the temperature of the liquor where boiling occurs. So a pound of steam boils less than one pound of water because some of the energy of the steam is required to preheat the feed. However, even if the feed were at the same temperature as the liquor, a pound of steam would boil less than one pound of water because the latent heat of the hot steam is less than the latent heat of the water being boiled.

OVERVIEW OF EVAPORATOR DESIGN

The design equation for evaporators can be summarized as

$$\text{heat duty:} \quad \underbrace{(\dot{m}_f - \dot{m})H_v}_{\text{vapor}} - \underbrace{\dot{m}_f H_f}_{\text{feed}} + \underbrace{\dot{m}H}_{\text{liquor}} = q = \underbrace{\dot{m}_s(H_s - H_c)}_{\text{steam}} \quad (21)$$

$$\text{HXer area:} \quad q = U A \Delta T_m$$

For preliminary designs, we can approximate

$$\Delta T_m \approx \text{const.} = T_s - T$$

where T is the boiling point of the liquor at the pressure in the vapor space. This is approximate when there is significant BPE because T will vary along the length of the heat exchanger tube as the concentration of solute also changes.

- Evaluation of enthalpies with negligible BPE and negligible heat of dilution (example on page 29 and also Example 8.4-1 on p498). Assuming the solvent is water, we can read the enthalpies of all three streams from the steam tables.

read T, T_s, H, H_f and H_v from steam tables

- Evaluation of enthalpies with complications (Example 8.4-3 on p501):

read H, H_f from special table or chart
read T from Dühring chart; T_s, H_v from steam tables*

* Since enthalpies are being taken from more than one source, we should take care that the reference state is the same for all tables and charts used in a given problem. The steam tables in Geankoplis use saturated liquid water at 32°F and 1 atm as the reference state. The enthalpy chart for NaOH solutions in Geankoplis also use 0 wt% NaOH at 32°F and 1 atm as the reference state.

COMPLICATIONS

Boiling-Point Elevation

Some complications arise in other evaporator problems because the enthalpy and partial pressure of a liquid more generally depends on its concentration as well as its temperature. Whenever a solute is added to water, the partial pressure of the water is reduced. Recall ***Raoult's law*** from thermodynamics.

Raoult's law:
$$p_i(x_i, T) = x_i p_i^o(T)$$

where

p_i = partial pressure of component i
 x_i = mole fraction component i
 p_i^o = vapor pressure of pure i at some T

Note that adding any solute with water causes $x_w < 1$ so that

$$p_w < p_w^o$$

In general, this implies that I must heat the solution up to a higher temperature (i.e. higher than the b.p. of pure solvent) before it will boil. This increase in boiling point due to addition of solute is called

boiling-point elevation (BPE) - increase in b.p. due to addition of solute

This effect can be quite significant for concentrated solutions of inorganic salts. For example, for at a pressure of 1 atm, the boiling point of pure water is

1 atm, 0% NaOH in water: $T_{bp} = 212^\circ\text{F}$

If the pressure is other than 1 atm, the temperature can be read from the steam tables. Given this boiling point for pure water, we can look up the boiling point of solutions of NaOH from a Dühring chart (see p500 of Geonkoplis):

50wt% NaOH in water: $T_{bp} = 283^\circ\text{F}$ at 1atm

Note that the boiling point of the solution is significantly greater than the boiling point of pure solvent. BPE is a colligative property, which means

colligative property -- depends on molar (not mass) concentration

Example: Use Raoult's law to estimate the partial pressure of water at 100°C of a) a 50wt% NaOH solution and b) a 50wt% suspension of "organic colloids" (use $MW_{\text{average}} = 1000 \text{ g/mol}$). Estimate the BPE for each.

Solution: To calculate the mole fraction of water in the solution, take 1 gram of solution as a basis. This 1 gram mixture consists of 0.5 g of water (MW = 18) and 0.5 g of NaOH (MW = 40). We calculate the corresponding number of moles of each and the mole fraction:

	NaOH (MW=40)	Organic Colloids (MW=1000)
x_w	$\frac{\frac{0.5\text{g}}{18\frac{\text{g}}{\text{mol}}}}{\frac{0.5\text{g}}{18\frac{\text{g}}{\text{mol}}} + \frac{0.5\text{g}}{40\frac{\text{g}}{\text{mol}}}} = 0.690$	$\frac{\frac{0.5\text{g}}{18\frac{\text{g}}{\text{mol}}}}{\frac{0.5\text{g}}{18\frac{\text{g}}{\text{mol}}} + \frac{0.5\text{g}}{1000\frac{\text{g}}{\text{mol}}}} = 0.982$

At 100°C (the b.p. of pure water), the vapor pressure of pure water is 1 atm ($= p_w^o$). Using Raoult's law, the partial pressure is estimated as

p_w	$0.690(1 \text{ atm}) = 0.690 \text{ atm}$	$0.982(1 \text{ atm}) = 0.982 \text{ atm}$
-------	--	--

To cause the solution to boil, the partial pressure must be raised to 1 atm. For the same mole fraction of NaOH, this means raising the vapor pressure to

p_w^o	$\frac{1 \text{ atm}}{0.690} = 1.450 \text{ atm}$	$\frac{1 \text{ atm}}{0.982} = 1.018 \text{ atm}$
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Using the steam tables (Appendix A.2-9), we find that the temperature has to be

T	110.0°C	100.8°C
-----	---------	---------

Thus using Raoult's law, the BPE is estimated to be

BPE from Raoult's law	$110.0^\circ\text{C} - 100^\circ\text{C} = 10.0^\circ\text{C}$	$100.8^\circ\text{C} - 100^\circ\text{C} = 0.8^\circ\text{C}$
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Of course, this is only an estimate. Raoult's law is only asymptotically correct as $x_w \rightarrow 1$. The actual BPE is 39°C.

BPE determined from Fig. 8.4-2	$283^\circ\text{F} - 212^\circ\text{F} = 71^\circ\text{F} = 39^\circ\text{C}$	—
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Although BPE is significant for a low-molecular-weight solute like NaOH, the same 50wt% concentration of an "organic colloid" (e.g. orange juice) may have a negligible BPE because the molecular weight is much higher. Thus the same wt% gives a much smaller molar concentration of a high-molecular-weight solute and therefore a much smaller BPE.

Heat of Dilution

If you dilute concentrated sulfuric acid by adding water, large quantities of heat can be released. If the mixing is adiabatic and both fluids are initially at room temperature, the final temperature after mixing can be high enough to causing boiling. You were probably warned to use great caution when diluting sulfuric acid in chemistry lab. The problem is that the enthalpy of a solution depends not only on its temperature, but also on its concentration:

$$H = H(T, c)$$

which means you might need more than just a heat capacity to calculate sensible heat changes. Fig. 8.4-3 gives the enthalpy-concentration diagram for NaOH solutions.

Example: Suppose we dilute 1-lb of 50wt% NaOH solution at 70°F with 1-lb of pure water, also at 70°F. What is the final temperature if the mixing is adiabatic?

Solution: read the enthalpies of the two solutions from 8.4-3:

$$\begin{aligned} H(50\%, 70^\circ\text{F}) &= 123 \text{ BTU/lb} \\ H(0\%, 70^\circ\text{F}) &= 40 \text{ BTU/lb} \end{aligned}$$

Multiplying each by the corresponding weight and adding, we obtain the final enthalpy of the mixture (“adiabatic” just means that no energy is lost during mixing):

$$(123 \text{ BTU/lb})(1 \text{ lb}) + (40 \text{ BTU/lb})(1 \text{ lb}) = 163 \text{ BTU}$$

Dividing by the mass of the final mixture, we obtain the enthalpy per pound:

$$\frac{163 \text{ BTU}}{2 \text{ lb}} = 81.5 \frac{\text{BTU}}{\text{lb}} = H(25\%, T = ?)$$

This represents the specific enthalpy of the final mixture, which we also know is 25wt%. Again using Fig. 8.4-3, to get this H , we need to choose the temperature as

$$T = 123^\circ\text{F}$$

Thus the final solution is warmer than the two initial solutions, due to the “heat of dilution.”

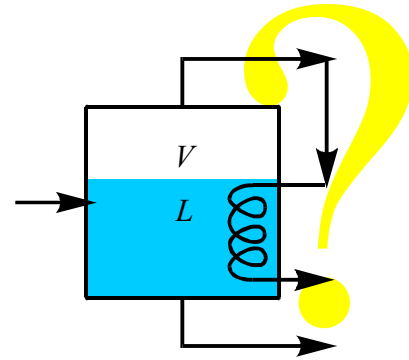
Question: when diluting sulfuric acid (which also exhibits a significant heat of dilution), why is it wiser to add (concentrated) acid to water, rather than water to (concentrated) acid?

We will now look at two methods to improve steam economy of an evaporator:

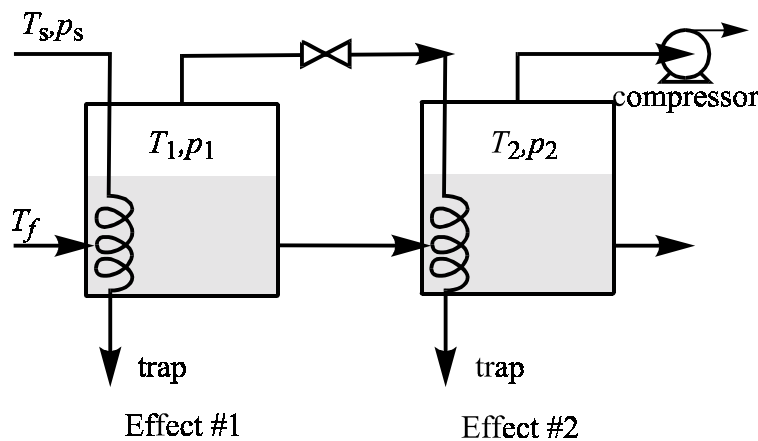
1. multiple “effects”
2. vapor recompression

MULTIPLE EFFECTS

In the simple evaporators we have dealt with so far, one of the product streams is water vapor — also known as steam. Why can't this vapor be used in place of steam? The answer is simple: if the vapor replaced the steam, there would be no driving force for heat transfer because the "steam" and the vapor would have the same temperature. To get a driving force in the right direction, we have to use steam with a higher pressure. One method of making use of the latent heat of the vapor is to compress it. We will look at that option below, but first let's examine another option.



One way to improve economy is to divide the heat duty among several evaporators which are piped together in such a way that the vapor produced by one can be used to boil the liquid in another. This reduces the steam usage and improves economy.



You can have any number of evaporators connected together in this way. Each evaporator in this sequence is called an *effect*, and the entire sequence is called a *multiple-effect evaporator*. In the figure above, we show a double-effect evaporator. In order to maintain a driving force for heat transfer in each effect, we must have

$$T_2 < T_1 < T_s$$

This can be accomplished by having* $p_2 < p_1 < p_s$

This requires a vacuum pump or compressor:

* Assuming we have saturated liquid and vapor in each effect, the pressure in any effect is just the vapor pressure at the temperature for that effect. Recall that vapor pressure increases with temperature.

$p_2 < p_1$: ♦

$$\Delta T_2 = T_1 - T_2 > 0$$

$$q_2 = U_2 A_2 \Delta T_2 \quad (22)$$

Of course, we still have to supply steam to the first effect

$$\Delta T_1 = T_s - T_1 > 0$$

$$q_1 = U_1 A_1 \Delta T_1 \quad (23)$$

For simple designs where BPE and ΔH_{dil} are negligible and where the sensible heat needed to preheat the feed up to its boiling point is negligible, the same latent heat added to the vapor in the first effect is recovered by condensing in the second effect:

$$q_1 \approx q_2 \quad (24)$$

Usually the pressure in the last effect and the pressure of the steam are known. Using the steam tables, we can convert these pressures into temperatures. The unknowns are the temperatures and pressure in the other effects.

Example: given T_s and T_2 , find T_1 . Solution: (22) and (23) into (24) yields

$$U_1 A_1 (T_s - T_1) = U_2 A_2 (T_1 - T_2)$$

This represents one equation in one unknown (T_1), assuming that the U 's and A 's are known.

If instead, we have N effects, the analog of (22), (23) and (24) yield $N-1$ equations in $N-1$ unknowns. These equations are strongly coupled. A simpler approach is to try and solve for the ΔT_i 's instead of the T_i 's. We will illustrate this by re-solving the last example. From (22) and (23), we have

$$\Delta T_1 = \frac{q_1}{U_1 A_1} \quad (25)$$

and

$$\Delta T_2 = \frac{q_2}{U_2 A_2} \quad (26)$$

Adding (14) and (26):

$$\sum_{i=1}^2 \Delta T_i = \frac{q_1}{U_1 A_1} + \frac{q_2}{U_2 A_2} \quad (27)$$

Dividing (25) by (27):

♦ The expression for ΔT which follows assumes that the vapor produced in the first effect condenses in the steam chest of the second effect at the same temperature at which it boiled. If BPE is significant, the vapor will condense at a lower temperature than it boiled (even if the pressure is the same). Why?

$$\frac{\Delta T_1}{\sum \Delta T} = \frac{q_1 / U_1 A_1}{q_1 / U_1 A_1 + q_2 / U_2 A_2} \stackrel{q_1 = q_2}{\Rightarrow} \frac{1 / U_1 A_1}{1 / U_1 A_1 + 1 / U_2 A_2} \quad (28)$$

Since $\sum \Delta T$ can be easily calculated from the info given in the problem statement:

$$\sum \Delta T = \Delta T_1 + \Delta T_2 = (T_s - T_1) + (T_1 - T_2) = T_s - T_2 \quad (29)$$

we can easily calculate ΔT_1 from (28):

$$\Delta T_1 = \frac{1 / U_1 A_1}{1 / U_1 A_1 + 1 / U_2 A_2} (T_s - T_2)$$

The analog of (24) - (29) for N effects are

$$(25): \quad \Delta T_i = \frac{q_i}{U_i A_i} \quad \text{for } i = 1, 2, \dots, N \quad (30)$$

$$\frac{\Delta T_i}{\sum \Delta T} = \frac{q_i / U_i A_i}{q_1 / U_1 A_1 + q_2 / U_2 A_2 + \dots + q_N / U_N A_N}$$

Applying the analog of (24) ($q_1 = q_2 = \dots = q_N \equiv q$), we can cancel out the q_i , leaving:

$$\frac{\Delta T_i}{\sum \Delta T} = \frac{1 / U_i A_i}{1 / U_1 A_1 + 1 / U_2 A_2 + \dots + 1 / U_N A_N} \quad (31)$$

Now the sum of the driving forces can also be expressed as

$$\begin{aligned} \sum \Delta T &= \Delta T_1 + \Delta T_2 + \dots + \Delta T_N \\ &= (T_s - T_1) + (T_1 - T_2) + \dots + (T_{N-2} - T_{N-1}) + (T_{N-1} - T_N) \\ &= T_s - T_N \end{aligned} \quad (32)$$

(32) into (31):

$$\Delta T_i = (T_s - T_N) \frac{1 / U_i A_i}{1 / U_1 A_1 + 1 / U_2 A_2 + \dots + 1 / U_N A_N} \quad \text{for } i = 1, 2, \dots, N$$

In the simple case in which all the A 's are equal and all the U 's are equal, this last result reduces to

$$\Delta T_i = \frac{1}{N}(T_s - T_N) \quad \text{for } i = 1, 2, \dots, N$$

In short, the total driving force is divided equally among each of the N effects.

Performance

Each effect results in the evaporation of water at a rate equal to q/λ_i . Summing the rate of evaporation in each effect, we obtain the total rate of evaporation:

$$\dot{m}_V = \sum_{i=1}^N \frac{q_i}{\lambda_i}$$

Steam is used only in the first effect. The rate of steam consumption in the first effect is

$$\dot{m}_s = \frac{q_1}{\lambda_s}$$

The steam economy can then be calculated as

$$\frac{\dot{m}_V}{\dot{m}_s} = \frac{\sum_{i=1}^N \frac{q_i}{\lambda_i}}{\frac{q_1}{\lambda_s}} \quad q_1 = q_2 = \dots = q_N \quad \Rightarrow \quad \lambda_s \sum_{i=1}^N \frac{1}{\lambda_i} \approx N$$

If we neglect changes in the latent heat with temperature and pressure, then all the λ 's are equal and the sum reduces to N . If changes in the latent heat with temperature are considered, the sum will be less than N .

Summary: For the same capacity, steam requirements are significantly less for multiple-effect evaporators, than for single-effect evaporators: generally, the economy increases with the number of effects. The price that is paid for this increased steam economy is greater equipment costs: generally the cost of the equipment is proportional to the number of effects.

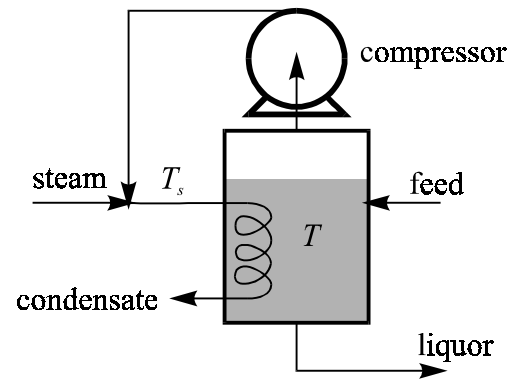
For a single effect: economy < 1

For N effects: economy < N

The reason that the economy increased is that we need to supply steam only to the first effect. The source of heat for 2nd, 3rd, ... N^{th} effects is supplied by condensing the vapor produced in the previous effect.

VAPOR RECOMPRESSION

Multiple effects recover some of the latent heat of the overhead vapor by using it in place of steam to boil the liquor in downstream effects. Is there any way we can use the vapor in place of steam in a single-effect evaporator? The problem with using the vapor in place of steam is that the temperature of the vapor is the same as the temperature of the liquor: the liquor and vapor leaving the same effect are already in thermal equilibrium with each other. In other words, there is no driving force for heat transfer.



without compression: $\Delta T = T_s - T = 0$

One way to increase the temperature of the vapor is to compress it. Fig. 1 shows how adiabatic compression of water vapor (treated as an ideal gas) increases its temperature.* Note that the temperature rises faster with increases in pressure than the boiling point increases. Thus adiabatic compression of a saturated vapor nearly always produces a superheated vapor. When heat is removed from this compressed vapor, it will eventually condense at its boiling point for that pressure.

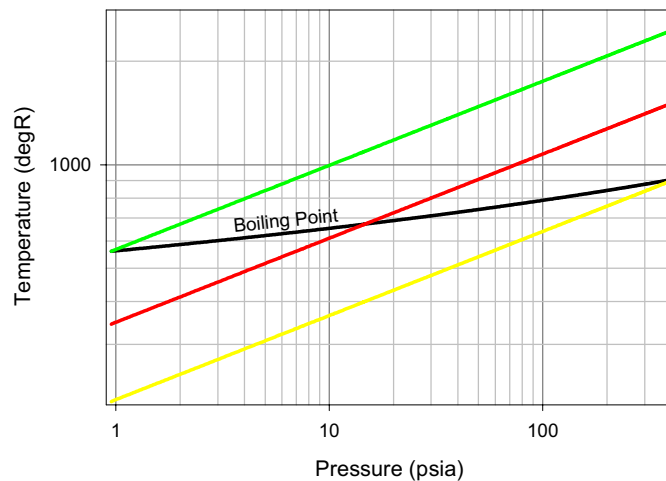


Fig. 1
Colored curves show how temperature increases with adiabatic compression, starting with saturated vapor at 1 psia (green), 14.7 psia (red) or 400 psia (yellow). For comparison, the boiling point is shown by the black curve.

Increasing the pressure of the vapor also increases its boiling point, so that as the vapor condenses, it stays at a high temperature T_s so we always have some driving force.

With compression: $\Delta T = T_s - T > 0$

Unfortunately, raising the temperature and pressure of the vapor actually lowers its latent heat per pound

$$\lambda_s < \lambda \text{ (because } T_s > T)$$

* Temperatures calculated from (7.30) in Smith & van Ness (4th ed., p237).

so the vapor no longer has enough latent heat to boil the same mass of liquid. Thus *make-up* steam is required, although generally much less steam is needed than if the vapor's latent heat is not recycled.

The reduction in steam is not without cost. We still have to pay the utilities (electricity or steam turbine) to operate the compressor. Generally, compressors are expensive to buy, maintain, and operate; so you have to do some economic calculations to see if using a compressor is economical. At the usual conditions of an evaporator, the vapor can be treated as an ideal gas. Then the work required for adiabatic compression can be estimated from ♦

$$W_{pr} = \frac{p_{in} \gamma}{(\gamma - 1) \rho_{in}} \left[\left(\frac{p_{out}}{p_{in}} \right)^{1 - 1/\gamma} - 1 \right] [=] \frac{\text{Btu}}{\text{lb}} \quad (33)$$

where “out” and “in” refer to the outlet and inlet of the compressor and where γ is the heat capacity ratio, which is

$$\gamma \equiv \frac{c_p}{c_v} = \frac{c_p}{\underbrace{c_p - \frac{R}{M}}_{\text{for ideal gas}}} \approx 1.324$$

for water vapor using

$$\begin{aligned} c_p &= 0.45 \text{ Btu/lb-}^\circ\text{F}, \\ R &= \text{ideal gas constant} = 1.986 \text{ Btu/lbmol-R} = 1.986 \text{ cal/mol-K} \\ M &= \text{mol. wgt.} = 18 \text{ lb/lbmol} = 18 \text{ g/mol} \end{aligned}$$

Now (33) gives the work needed to compress a unit mass of gas, under ideal conditions (no irreversible losses of energy). To get the power requirements, we must multiply by the mass flow rate and divide by the mechanical efficiency (η) of the compressor:

$$P = \frac{(\dot{m}_f - \dot{m}) W_{pr}}{\eta} [=] \frac{\text{Btu}}{\text{hr}} [=] \text{kW}$$

By compressing the vapor to raise its temperature, we are lowering its latent heat of vaporization. This means that, even if we completely condense all the vapor, we still won't have enough latent heat to boil the liquor at its lower temperature. The difference must come from make-up steam. To estimate the make-up steam requirements, let's return to the design equation (19) for the total heat duty:

♦ See Smith & van Ness, 4th ed., footnote on page 238.

$$q = \underbrace{(\dot{m}_f - \dot{m})H_v}_{\text{vapor}} - \underbrace{\dot{m}_f H_f}_{\text{feed}} + \underbrace{\dot{m}H}_{\text{liquor}}$$

In the simple case where BPE and ΔH_{dil} are negligible (i.e. for inorganic colloids), H_f and H differ from the enthalpy of saturated liquid only in sensible heat. To the extent that sensible heat is negligible,* we can substitute the enthalpy of saturated liquid for H_f and H :

$$\begin{aligned} q &= (\dot{m}_f - \dot{m})H_v - \dot{m}_f H_L + \dot{m}H_L \\ &\approx (\dot{m}_f - \dot{m})H_v - (\dot{m}_f - \dot{m})H_L \\ &= (\dot{m}_f - \dot{m})(H_v - H_L) \\ &= (\dot{m}_f - \dot{m})\lambda \end{aligned}$$

heat to boil vapor:
$$q \approx (\dot{m}_f - \dot{m})\lambda \quad (34)$$

This heat duty is partially offset by the latent heat recovered by condensing the compressed vapor. The remainder comes from **make up steam**:

$$q = \underbrace{(\dot{m}_f - \dot{m})\lambda_s}_{\text{compressed vapor}} + \underbrace{\dot{m}_s \lambda_s}_{\text{make-up steam}} \quad (35)$$

where we are assuming we are compressing the vapor to the same pressure as the make-up steam. Eliminating q between (34) and (35), we can solve for the steam requirements:

$$\dot{m}_s \approx (\dot{m}_f - \dot{m}) \left(\frac{\lambda}{\lambda_s} - 1 \right)$$

Notice that any compression allows us to recover all the latent heat of the vapor, thus significantly reducing steam consumption without compression. However greater compression actually increases steam consumption (because λ_s decreases with pressure). Rearranging this expression, we can calculate the economy:

$$\frac{\dot{m}_f - \dot{m}}{\dot{m}_s} \approx \frac{\lambda_s}{\lambda - \lambda_s} \gg 1$$

* Sensible heat is often negligible compared to latent heat. To see why, note that the latent heat of vaporization of water at 1atm, 212°F is 970.3 btu/lb, where 1 btu is the amount of sensible heat required to raise the temperature of one lb of water 1°F. This means that, for sensible heat to equal latent heat, I need to raise the temperature of water 970°F. A temperature rise of only 30°F, say, represents a sensible heat change of 30/970 or 3% of the latent heat of water. This is an estimate of the relative error made in this estimate of \dot{m}_s .

which is now very much greater than unity. However, this way of computing economy is unfair because the reduction in steam consumption is at the cost of operating the compressor. In computing the “economy” for an evaporator with vapor recompression, it is customary to add an equivalent steam rate for the compressor to the make-up steam rate before dividing into the capacity.

- If the plant uses a steam-powered turbine or if the plant uses steam generators to make its own electricity, then the apparent steam usage is

$$(\dot{m}_s)_{app} = \dot{m}_s + \frac{P}{\lambda'_s \eta_s} [=] \frac{\text{btu/hr}}{\text{btu/lb}} [=] \frac{\text{lb}}{\text{hr}}$$

where P is the electrical power supplied to the compressor, λ'_s is the latent heat of the steam used (the prime is added because the pressure of the steam used here might be different from that used in the evaporator) and η_s is the efficiency of electricity generation from steam (typically 0.35).

- On the other hand, if electricity is purchased from a utility to drive the compressor, then it makes sense to convert the electricity usage into an equivalent amount of steam (on a financial basis):

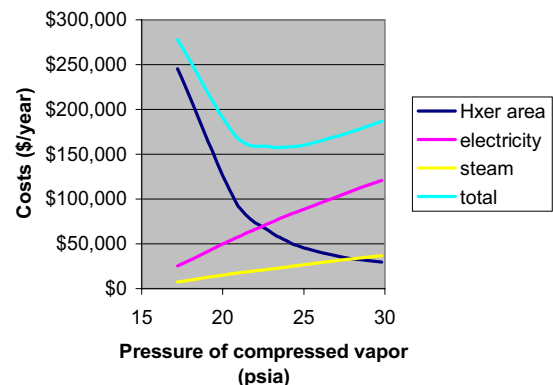
$$(\dot{m}_s)_{app} = \dot{m}_s + P \times \frac{\$/\text{kW} \cdot \text{hr}}{\$/\text{lb of stm}}$$

If P is in kW then the last term yields lb/hr of steam.

Regardless of which method of converting the power usage is appropriate, the economy is computed as:

$$\text{economy} \equiv \frac{\dot{m}_f - \dot{m}}{(\dot{m}_s)_{app}}$$

In Hwk #3, Prob. 5, we will consider the trade off of operating costs (direct steam usage plus electricity for compressor) and capital costs (heat exchanger area) as a function of the output pressure of the compressor. The results are summarized in the graph at right, which shows that an optimum pressure exists at which total costs are minimized. Notice that both power requirements for the compressor as well as steam usage increase with pressure. Only when the cost of the heat exchangers is considered does an optimum exit.



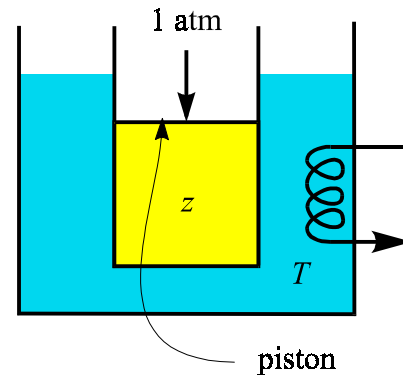
Chapter 6. Vapor-Liquid Equilibrium

Reference: Smith & Van Ness, 4th Ed., Sect. 10.5

Today we switch from heat-transfer operations (heat exchange, evaporation, condensation) to mass-transfer operations (distillation, extraction, absorption, humidification). Instead of sizing equipment to exchange *heat* between two phases we will size equipment to exchange *mass* between two phases.

NO. OF PHASES PRESENT

Suppose I have an apparatus like that shown in the figure at right in which I can place an arbitrary mixture of components and control the temperature and pressure. How many phases will be present at equilibrium?

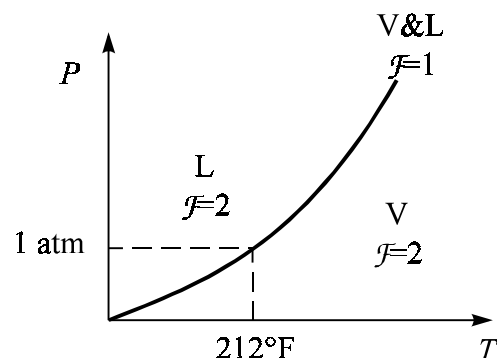


One Component

For example, suppose I put just water in the piston at 1 atm and room temperature (say 70 °F). Just one component — no air! Is the water liquid, solid, or vapor? We know from our own experience that water is a liquid near room temperature. Thus we have just one phase present at equilibrium.*

If I repeated this experiment at 250 °F, we would have the water present as all vapor — again I have just one phase present. Only if the temperature corresponds to the **boiling point** (212 °F) will I have two phases present. If I repeated the experiment at some other pressure there will be only one temperature at which two phases are present.

The relationship between temperature and pressure for which two phases co-exist at equilibrium is called the **vapor pressure** curve. This diagram summarizes all the vapor-liquid phase behavior for a one-component system.



Two Components

Now suppose I put two components in the pot: let's say a mixture of *n*-heptane (C_7) and *n*-octane

* If air were present as a second component, we would also have a gas phase.

(C₈), which are important components in gasoline. The vapor-liquid phase behavior of two-component systems is a little more complicated, because I have an additional variable — composition — as well as T and P . Instead of a single temperature at which both liquid and vapor can co-exist, there is a range of temperatures.

At a given pressure, we can summarize the phase behavior by means of a T_{xy} diagram like that shown at right. To understand the meaning of this diagram, consider what happens if we charge the piston with a mixture of heptane and octane having a particular composition. If the temperature is low enough, we will have just one phase: liquid.

As we heat this mixture to the temperature corresponding to the lower curve, we would begin to see bubbles of vapor formed in the liquid as more heat is added. This temperature at which the bubbles first form is called the

bubble point — when heating a subcooled liquid, the temperature at which the first bubble forms

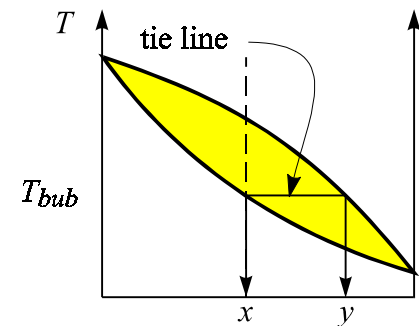
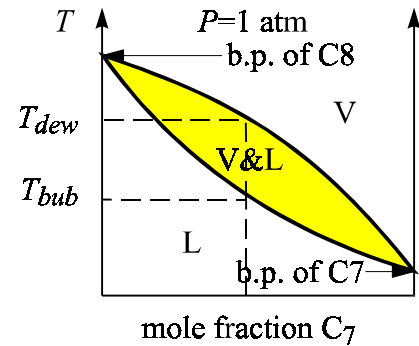
The composition of this first bubble can also be read from the T_{xy} diagram. In general, the vapor will be richer than the liquid in one component and leaner in the other. This difference in composition of the vapor and liquid can serve as the basis for separating two or more components of a mixture. By completely condensing the vapor, I produce a liquid which is richer in one component than the original liquid. Thus I have achieved a degree of separation of the two components.

For a binary system having two phases, we denote the composition of the liquid and vapor using x and y :

x = mole fraction of more volatile component* in liquid phase

y = mole fraction of more volatile component in vapor phase

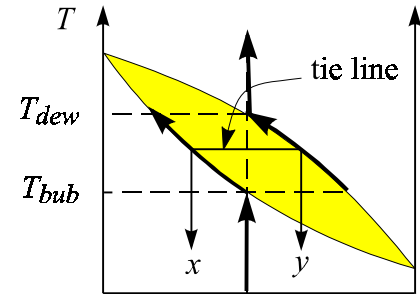
Keep in mind that liquid and vapor must have the same temperature at equilibrium. The line connecting the two points representing vapor and liquid is called a **tie line**. It's horizontal on a T_{xy} diagram.



* By “more volatile component” we mean that component which has either 1) the higher vapor pressure at a given temperature, or 2) the lower boiling point for a given pressure. Example: for a mixture of C₇ (heptane) and C₈ (octane), heptane has the lower normal boiling point and so heptane is the more volatile component.

As we continue to heat the mixture, the liquid becomes less rich in the more volatile component since the more of the more volatile component is leaving for the vapor phase. The compositions of the liquid and vapor move along the heavy solid line shown in the figure at right. The highest temperature at which liquid remains is called the

dew point — when cooling a superheated vapor, the temperature at which the first drop of dew forms



Eventually, as we continue to heat, all the mixture ends up in the vapor. ♦

IDEAL SOLUTIONS OBEY RAOULT'S LAW

Reference: Smith & Van Ness, Example 10.1 (p305)

Now let's try to predict the Txy diagram for the simplest case: an ideal solution in equilibrium with an ideal gas. So let's suppose we are at some temperature for which both phases co-exist at equilibrium.

Let

$$P_i' = \text{vapor pressure of pure } i$$

$$P = \text{total pressure}$$

$$x_i, y_i = \text{mole fractions in liq or vapor at equil.}$$

$$p_i \equiv y_i P = \text{partial pressure of component } i$$

Raoult's law:

$$p_i = x_i P_i'$$

IDEAL BINARY MIXTURES

What we have said so far about ideal solutions applies to any number of components. Let's now restrict our attention to systems with only two components, which we will call A and B.

The mole fractions must sum to one for each phase, so we can express the mole fraction of B in terms of that for A:

$$x_B = 1 - x_A$$

♦ The vertical line in left margin indicates that this material was not covered during class. I do however expect you to read it and you will be responsible for this material on the exams.

vapor	y_i
liquid	x_i

$$y_B = 1 - y_A$$

Applying Raoult's law to each component:

$$p_A = y_A P = x_A P_A' \quad (36)$$

$$p_B = (1 - y_A) P = (1 - x_A) P_B' \quad (37)$$

Adding the partial pressures from (36) and (37) we obtain the total pressure:

$$P = p_A + p_B = x_A P_A'(T) + (1 - x_A) P_B'(T)$$

Solving for the mole fraction x_A : $x_A = (P - P_B') / (P_A' - P_B')$ (38)

from (36): $y_A = x_A P_A' / P$ (39)

Keep in mind that the vapor pressures in these equations depend on temperature. So if you specify a T and P , I can determine the vapor pressures and calculate the composition of the vapor and liquid which will be at equilibrium.

Given: T, P

Look up: $P_A'(T)$ and $P_B'(T)$

Calculate: x_A, y_A from (38) and (39)

Thus I can construct a complete phase diagram for the mixture using only vapor-pressure data for the pure components.

Example.♥ n -heptane and n -octane form a nearly ideal mixture. Use Raoult's law to construct a phase diagram at constant pressure (1 atm).

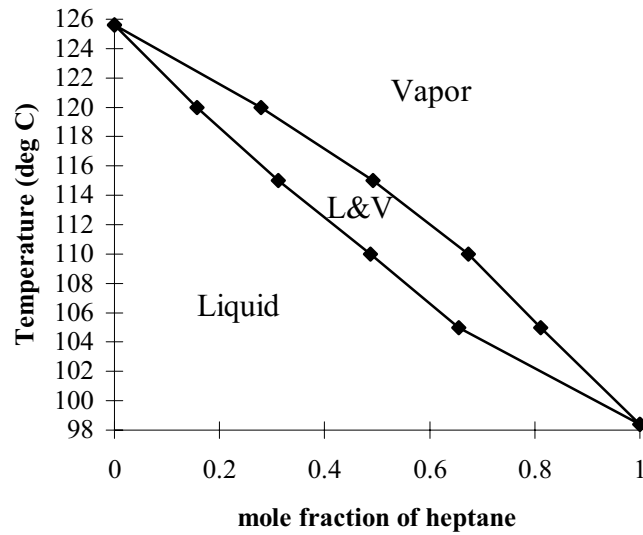
Solution. We first look up the normal boiling points of the two pure components.

component	T_{bp} (°C)	denoted by
n -heptane	98.4	A
n -octane	125.6	B

♥ Illustration 9.1 from Treybal. A similar example is 10.1 from S&VN (p305).

We choose the "low boiler" as component A since it has the larger vapor pressure over this range of temperatures. Next, we choose a temperature between the two boiling points, look up vapor pressures of the pure components and substitute into (38) and (39). The results are summarized in the table at right and the graph below.

T ($^{\circ}\text{C}$)	P'_A (mmHg)	P'_B (mmHg)	x	y	α
98.4	760	333	1.000	1.000	2.28
105	940	417	0.656	0.811	2.25
110	1050	484	0.488	0.674	2.17
115	1200	561	0.311	0.492	2.14
120	1350	650	0.157	0.279	2.08
125.6	1540	760	0.000	0.000	2.03



XY AND TXY DIAGRAMS

The Txy diagram is a convenient graphical method for summarizing vapor-liquid equilibrium (VLE) data at a particular pressure. For binary mixtures, we usually denote the mole fraction of the more volatile component as x in the liquid phase as y in the vapor phase. For this particular choice of x and y , the Txy diagram will always slope downward as shown at right.

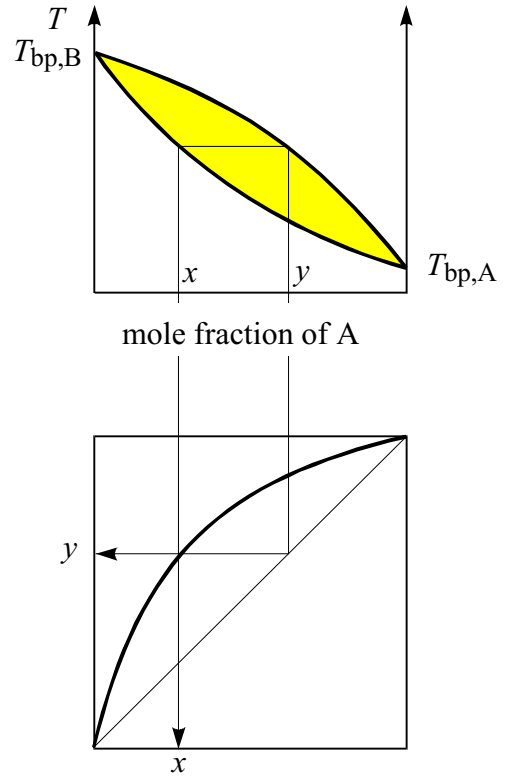
From the Txy diagram, one can construct an “xy” diagram, which is the one we will use in distillation calculations. The xy diagram is shown at right. For xy diagrams which resemble is one, the relationship between x and y can be sometimes be represented by a single number: the *relative volatility*, which is defined as

$$\alpha_{ij} \equiv \frac{K_i}{K_j}$$

where the K 's are called the *distribution coefficient*, which in turn are defined as:

$$K_i \equiv \frac{y_i}{x_i}$$

Since this term is also useful in mixtures having more than two components, we will use subscripts to denote components. Generally the most volatile component will have the largest distribution coefficient and will have its concentration increased (in the vapor compared to the liquid) by the largest percentage. The ratio of the distribution coefficients of two components is the relative volatility.



NONIDEAL BEHAVIOR

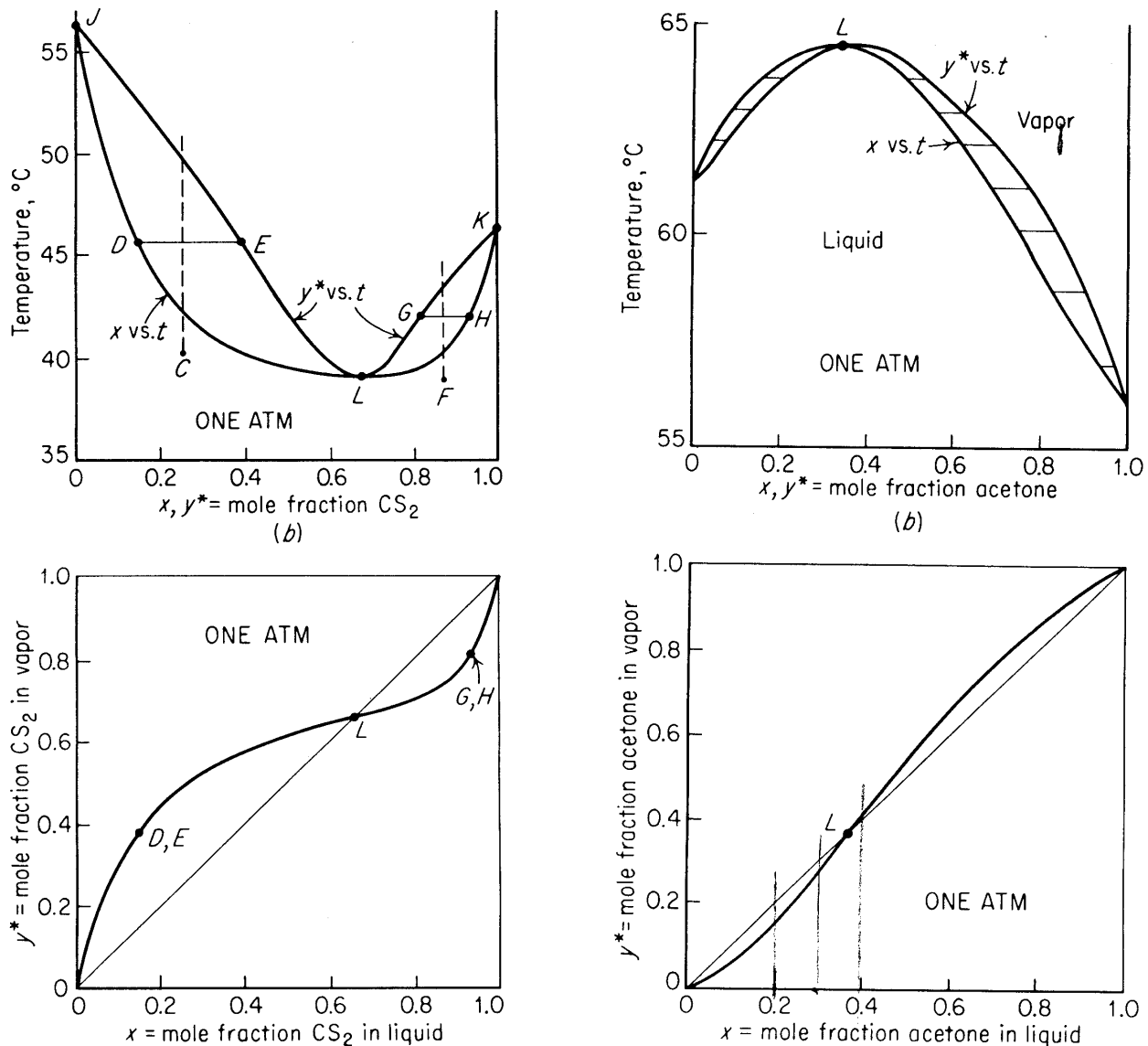


Fig. 2. Txy and xy diagrams for nonideal systems. On left is carbon disulfide in acetone at one atmosphere pressure. On right is acetone in chloroform. Taken from Treybal, 2nd ed., pages 290 and 295.

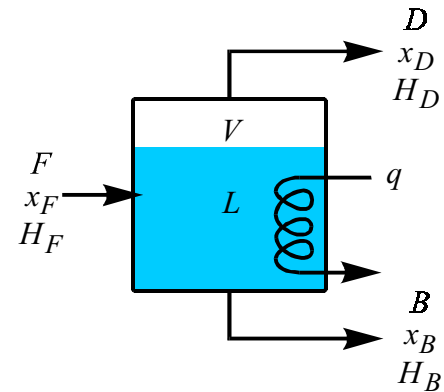
Examples Txy and xy diagrams for binary mixtures which display significant nonideal behavior are illustrated in Fig. 2. In particular notice that the curve on the xy-diagram can cross the 45° line. This point of crossing is called an *azeotrope*:

azeotrope - vapor and liquid have the exactly the same composition at equilibrium (i.e. $y = x$)

The occurrence of azeotropes can pose difficulty for distillation since producing a new phase by condensation or by evaporation produces no separation of components.

Chapter 7. Flash Distillation

Now let's apply these concepts about vapor-liquid equilibria to distillation. The simplest device for continuous distillation of some liquid feed is the "flash unit." This is just a HXer to add enthalpy of the feed and a chamber to allow the vapor and liquid to separate. The schematic at right is the same as that used for evaporation, however the vapor now contains all of the components — not just the "solvent".



Given the feed composition and the amount of heat added to the feed, we would like to determine the composition and flowrates of the distillate and bottoms products.

Given: F, x_F and q

Find: D, B, y_D and x_B

The mole and enthalpy balances are: $F = D + B$ (40)

$$x_F F = y_D D + x_B B \quad (41)$$

$$H_F F + q = H_D D + H_B B \quad (42)$$

where F, D, B are total molar flowrates of each stream and x and y are mole fractions of the more volatile component. The remaining equation comes from requiring the vapor and liquid products to be at equilibrium:

$$(x_B, y_D) \text{ lies on equil. curve} \quad (43)$$

(40)-(43) represent four equations in the four unknowns.

APPROXIMATE SOLUTION

The solution to these four equations can be obtained in a number of ways. Let's start with the simplest method. In many cases, the molar heat of vaporization is nearly the same for both components. (For this reason, we tend to solve all distillation problems using mole fraction rather than mass fractions, and express enthalpies per unit mole rather than enthalpy per unit mass.) If you can assume that the molar heat of vaporization of the mixture is completely independent of its composition, then solution is quite easy:

- Assume $H_D - H_B = \text{const}$, say ΔH_v [=] Btu/mol (independent of y_D)
- neglect sensible heat compared to latent heat

Let's choose saturated liquid having the composition of the feed as our reference state for enthalpies. Then

$$H_F = H_B = 0$$

and

$$H_D = \Delta H_v$$

Even if the liquid is not saturated liquid, its enthalpy differs from that of saturated liquid only through sensible heat, which is neglected here. The first equality is the result of neglecting sensible heats

Then (42) reduces to:
$$q \approx \Delta H_v D \quad (44)$$

Now we can define and solve for the fraction of the feed that is vaporized:

$$f \equiv \frac{D}{F} \approx \frac{q}{\Delta H_v F}$$

which can be considered known. We will now express the molar flowrates in terms of this f :

Dividing (40) by F and rearranging:
$$\frac{B}{F} = 1 - \frac{D}{F} = 1 - f \quad (45)$$

Dividing (41) by F :
$$x_F = y_D f + x_B (1 - f) \quad (46)$$

Solving for y_D :
$$y_D = \frac{f - 1}{f} x_B + \frac{x_F}{f} \quad (47)$$

which is a straight line on the xy diagram. To plot this line, we need to know the slope and one point which lies on the line.

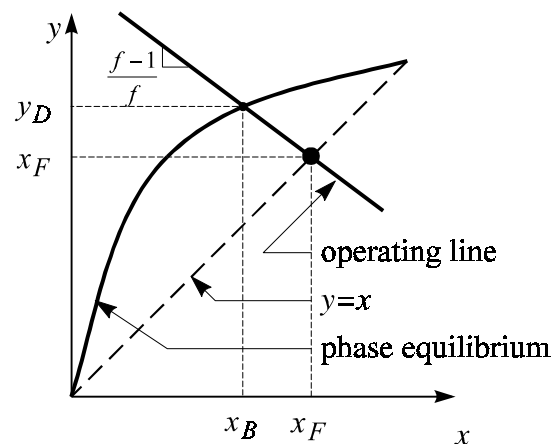
$$\text{slope} = \frac{f - 1}{f}$$

To obtain one point, we can substitute an arbitrary value in for x_B , say we substitute $x_B = x_F$. Then (47) becomes

$$y_D = \frac{f - 1}{f} x_F + \frac{x_F}{f} = x_F$$

Thus one point on the line given by (47) is

one point:
$$(x_B, y_D) = (x_F, x_F)$$



Knowing one point and the slope, we can draw the line. In effect, this line represents the relationship between y_D and x_B which is imposed by the mass and energy balances for a given q (or a given f) and for the given assumptions on calculating enthalpy. We call this line the

operating line: relationship between y_D and x_B which is imposed by the mass and energy balances

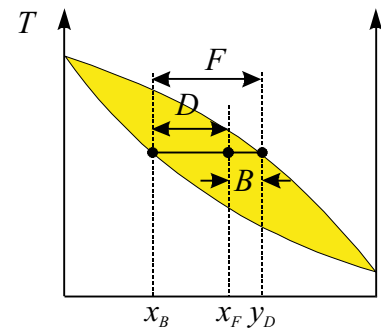
To find which point on this line is the solution for a given q , we need also to satisfy (43), which represents phase equilibrium. This relationship is a curve on the xy diagram, known as the

equilibrium curve: relationship between y_D and x_B which is imposed by vapor-liquid equilibria

The intersection of operating line and the equilibrium curve satisfies all four of the original equations and yields the answer.

Inverse Lever-Arm Rule on Txy Diagram

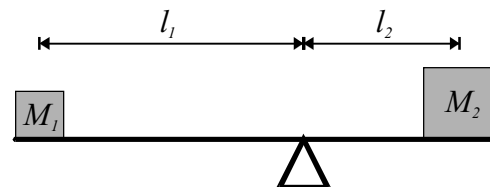
There is also a simple graphical procedure for estimating the fraction vaporized on a Txy diagram. Suppose you are given a feed composition and (instead of specifying the fraction evaporated) the final temperature of the mixture at equilibrium. Then you can locate a point (x_F, T) on the Txy diagram. A horizontal line through this point intersects the vapor and liquid curves at the composition of those phases: (x_B, T) and (y_D, T) .



As it turns out, the amount of vapor produced is inversely proportional to the distance between the feed point (x_F, T) and the vapor point (y_D, T) . Similarly, the amount of liquid remaining is inversely proportional to the distance between the feed point (x_F, T) and the liquid point (x_B, T) . More precisely, the ratio of vapor D to liquid B flowrates in an continuous flash unit is given by

$$\frac{D}{B} = \frac{x_F - x_B}{y_D - x_F} \quad (48)$$

where D , B and F are proportional to the distances indicated on the Txy diagram above. Because of the inverse nature of this relationship, this is called the **inverse lever-arm rule**. As a useful analogy, think of the flowrates as being like masses being balanced on a beam, resting on a fulcrum (see sketch at right). The further the mass is from the pivot, the smaller the mass can be. At (mechanical) equilibrium:



$$M_1 l_1 = M_2 l_2 \quad \text{or} \quad \frac{M_1}{M_2} = \frac{l_2}{l_1}$$

Notice the inverse relationship between the mass and the distance from the pivot. Now we will try to prove (48):

Proof:

Solving (46) for f :

$$f \equiv \frac{D}{F} = \frac{x_F - x_B}{y_D - x_B} \quad (49)$$

Substituting into (45):

$$\frac{B}{F} = 1 - \frac{D}{F} = 1 - \frac{x_F - x_B}{y_D - x_B} = \frac{y_D - x_F}{y_D - x_B} \quad (50)$$

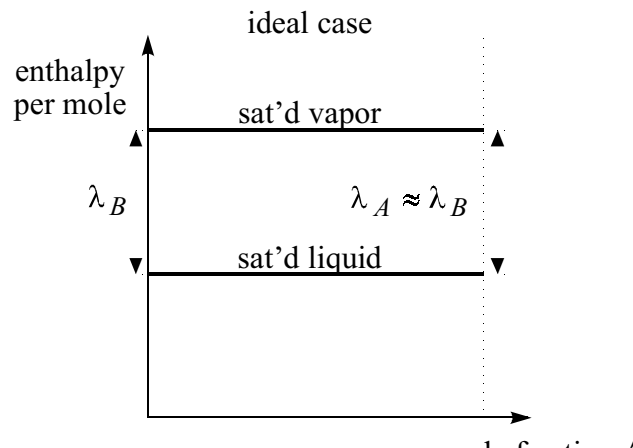
Dividing (49) by (50), we obtain (48).

RIGOROUS SOLUTION

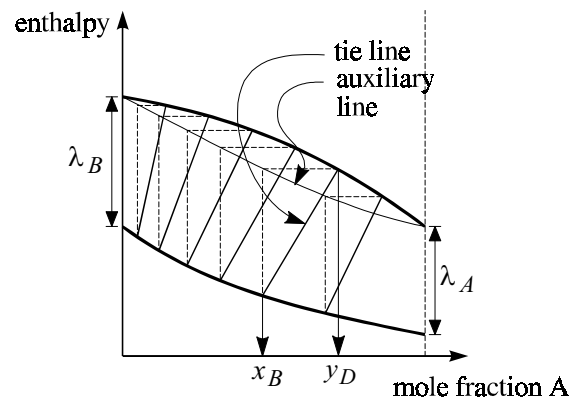
Although the approximate solution works reasonable well for some mixtures, for others it might not be good enough. Then you will need a lot more thermodynamic data besides latent heat and heat capacity. You will need an ***Hxy*** diagram.

An *Hxy* diagram is at least superficially similar to a *Txy* diagram in that it gives you some idea of the thermal condition of the mixture as a function of composition, except that instead of T on the y -axis, we have H .

At right we show the *Hxy* diagram which would apply if 1) the molar heats of vaporization of the two components are equal, and 2) sensible heat is negligible compared to the latent heat: two parallel, horizontal lines. Below it is an *Hxy* diagram for a real mixture.



Unlike a *Txy* diagram, the saturated liquid and saturated vapor curves do not connect at the ends or at any other composition. The vertical distance between these two curves represents the latent heat of vaporization at a particular composition, which is usually substantial for all compositions. Unlike temperature, enthalpy of liquid and vapor will be quite different, so the ***tie lines*** are not horizontal



like on a Txy diagram. In fact, tie lines tend to be more nearly vertical.

As we shall soon see, we will need to determine the tie line through a particular point. No matter how many tie lines your graph has, it would be a real stroke of luck if one passes through the particular point specified. So we need some way to interpolate tie lines. This is accomplished by means of:

auxiliary line -- a curve on an Hxy diagram for interpolating tie lines

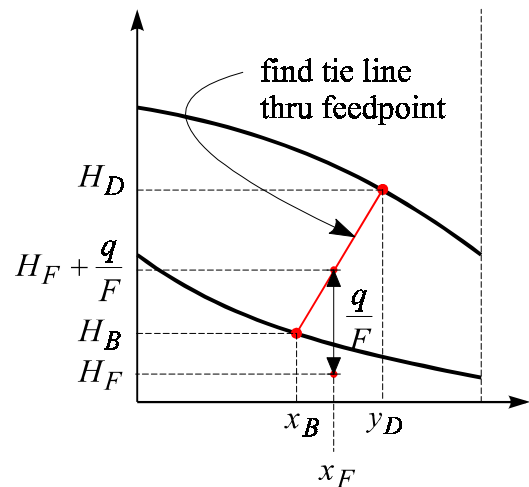
If we form a right triangle out of each tie line, then the locus of the points where the right angle is located is the auxiliary line. Of course, the ends of the auxiliary line coincides with the ends of the saturated vapor line. By reversing this procedure, we can locate more tie lines.

Now let's see how this diagram can be use do solve our flash distillation problems. First, I will give you the recipe and then later I will show why the recipe works.

recipe:

- locate the feed point (x_F, H_F)
- locate a second point q/F above the feed point $(x_F, H_F + q/F)$
- find the tie line which passes through this second point
- ends of the tie line are (x_B, H_B) and (y_D, H_D) .
- f can be determined with the help of (49):

$$f = \frac{z_F - x_B}{y_D - x_B}$$



Proof: now let's show that this procedure really works.

The main idea which we need to prove is that the point $(x_F, H_F + q/F)$ [call this point "F"] lies on the tie line. We know that (x_B, H_B) [call this point "B"] and (x_D, H_D) [call this point "D"] lie on the tie line since the two streams leaving the flash unit must be in phase equilibrium with each other. Our approach will be show that the slope of the line drawn from B to F is the same as the slope of the tie line drawn from F to D.

Substituting (40) into (41): $x_F(D+B) = y_D D + x_B B$

Dividing by D and solve for B/D : $\frac{B}{D} = \frac{y_D - x_F}{x_F - x_B}$ (51)

Divide (42) by F :

$$H_F + \frac{q}{F} = \frac{D}{F} H_D + \frac{B}{F} H_B$$

Using (40) to eliminate D :

$$H_F + \frac{q}{F} = \left(1 - \frac{B}{F}\right) H_D + \frac{B}{F} H_B = H_D - \frac{B}{F} (H_D - H_B)$$

Solving for B/F :

$$\frac{B}{F} = \frac{H_D - \left(H_F + \frac{q}{F}\right)}{H_D - H_B} \quad (52)$$

If instead, we had used (40) to eliminate B :

$$\frac{D}{F} = \frac{\left(H_F + \frac{q}{F}\right) - H_B}{H_D - H_B} \quad (53)$$

(52) \div (53):

$$\frac{B}{D} = \frac{H_D - \left(H_F + \frac{q}{F}\right)}{\left(H_F + \frac{q}{F}\right) - H_B} \quad (54)$$

Equating (51) and (54), we could show that:

$$\frac{H_D - \left(H_F + \frac{q}{F}\right)}{y_D - x_F} = \frac{\left(H_F + \frac{q}{F}\right) - H_B}{x_F - x_B}$$

Note that both sides of this equation have the form of rise/run on an Hxy diagram; thus each side represents the slope of a line drawn between two points on an Hxy diagram. These two slopes involve three distinct points:

$$(x_B, H_B); (x_F, H_F + q/F); \text{ and } (y_D, H_D)$$

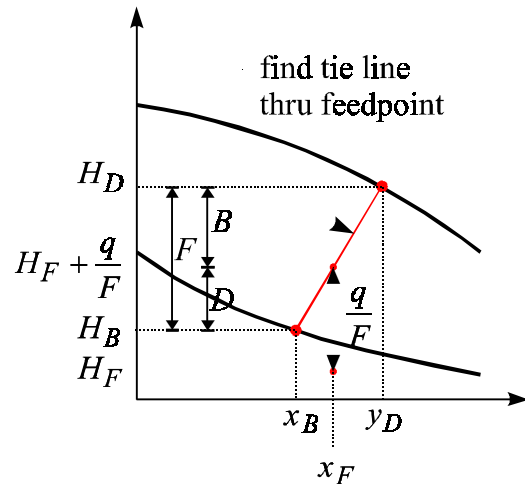
The equality of these two slopes means that these three points must lie on the same line. That line connecting B and D must be a tie line. The conclusion is that

$$(x_F, H_F + q/F) \text{ lies on tie line}$$

This is the basis for the receipt.

Inverse Lever-Arm Rule on Hxy Diagram

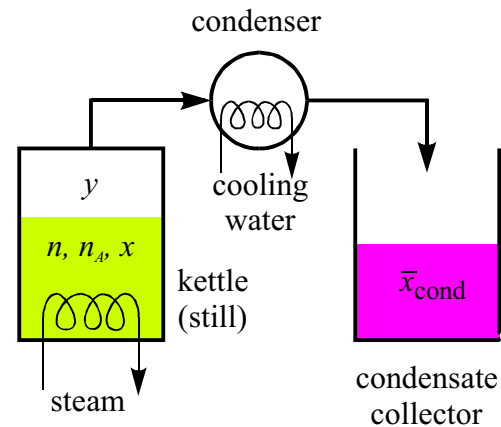
(54) provides a basis for an inverse lever-arm rule which is similar to (48). The total difference in enthalpy between saturated vapor and saturated liquid is $H_D - H_B$.[♦] This difference can be partitioned into $(H_F + q/F) - H_B$ and $H_D - (H_F + q/F)$. Thus the red tie line can be divided into two parts which are proportional to this difference in enthalpies. (54) says that ratio of the lengths of these two parts of the tie line equal the molar flowrate ratio B/D .



BATCH (DIFFERENTIAL) DISTILLATION

The oldest device for distillation consisted of a kettle into which a liquid mixture was placed. By heating the kettle either by fire or steam or electrically, the liquid is partially vaporized. After condensing the vapor, you have a product which is richer in one of the components.

If both of the components are volatile (e.g. ethanol and water), it wouldn't make sense to vaporize all of the liquid in the kettle. A mass balance can tell you that, if you vaporize the entire charge, the cumulative condensate composition will be essentially the same as the initial charge. Oh, perhaps you have removed some nonvolatile minerals which might have been in the water, but you won't enrich the ethanol concentration in this way. And enriching the composition of the more volatile component is the objective of distillation.



The solution is to evaporate only partially, because the first vapors which come off will be the richest in the more volatile component. Vapors produced later will only dilute the condensate. This process is called **batch distillation** because we process one batch at a time rather than continuously processing as with flash distillation.

Let's now try to predict how the composition of the liquid and vapor change as we evaporate more and more of the charge.

Let $n_A(t), n_B(t)$ = moles of component A or component B left in liq.

$$n(t) = n_A(t) + n_B(t) = \text{total moles of liq. left in kettle at time } t$$

[♦] $H_D - H_B$ is not the "heat of vaporization", which is the heat to totally vaporize one mole of feed. On the Hxy diagram, heat of vaporization is the length of a vertical line between the two curves.

$$x(t) = \frac{n_A(t)}{n(t)} = \text{mole fraction of A in liq. remaining} \quad (55)$$

$y(t)$ = instantaneous mole fraction of vapor produced

Suppose we evaporate a small amount of liquid at time t over a time interval dt :

$$n(t+dt) - n(t) = dn < 0$$

$-dn$ = total moles evaporated in time dt

A fraction of this is component A:

$$-dn_A = y(-dn) \quad (56)$$

(55) into (56):

$$-d(xn) = y(-dn)$$

$$x dn + n dx = y dn$$

$$n dx = (y-x) dn$$

$$\frac{dn}{n} = \frac{dx}{y-x}$$

Integrating from $t=0$, at which time x, n have their initial values:

$$x(0) = x_0 \quad \text{and} \quad n(0) = n_0$$

to some later time, at which time x, n have values:

$$x(t) \quad \text{and} \quad n(t)$$

we obtain

$$\int_{n_0}^{n(t)} \frac{dn}{n} = \int_{x_0}^{x(t)} \frac{dx}{y-x}$$

Integrating:

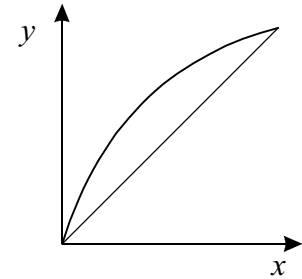
$$\ln \frac{n_0}{n(t)} = \int_{x(t)}^{x_0} \frac{dx}{y-x}$$

Solving for $n(t)$:

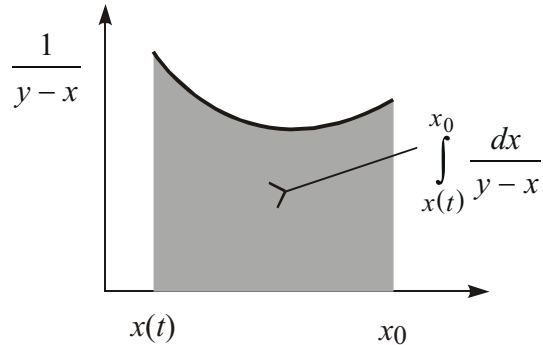
$$n(t) = n_0 \exp \left[- \int_{x(t)}^{x_0} \frac{dx}{y-x} \right]$$

which is called **Rayleigh's equation**. This serves as the design equation for batch distillation. To use this equation, we must recall that the vapor coming out of the kettle at any time is in equilibrium with the remaining liquid:

at equilibrium: $y = f(x)$



For each x between $x(0)$ and $x(t)$, we can look up the corresponding $y(t)$ and compute the integrand in Rayleigh's equation $1/(y-x)$. The integral is the area under the curve between these two limits.



Example: A 50mol% mixture of heptane and octane is placed in a batch and heated. Plot the composition of the remaining liquid as a function of the fraction of the initial charge which remains. At the pressure in the still, the vapor-liquid equilibrium can be reasonably represented by a constant relative volatility of $\alpha = 1.7$ (for a discussion on when this might arise, see p105).

Solution: For binary solutions, it's customary to define x and y to be the mole fraction of the more volatile component (heptane in this case); this choice yields relative volatilities greater than unity.

We will have to guess values of $x(t)$. Below we go through the procedure for one particular guess, say $x=0.2$.

Step 1: Guess x . We expect the vapor to be richer in the more volatile component

Step 2: Calculate the corresponding y . Recalling the definition of relative volatility (see page 51):

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j} = \frac{y/x}{(1-y)/(1-x)}$$

Dropping the subscripts and solving for y :

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

This function is evaluated for $\alpha=1.7$ and plotted in the figure at right. For $x=0.2$, this yields, $y=0.298$.

Step 3: We evaluate n/n_0 from Rayleigh's equation:

$$\frac{n(t)}{n_0} = \exp \left[- \int_{0.2}^{0.5} \frac{dx}{y-x} \right]$$

The integral is evaluated by assuming x 's between $0.2 < x < 0.5$. The integrand is plotted in the figure at right. The area under the curve between the two dotted lines is

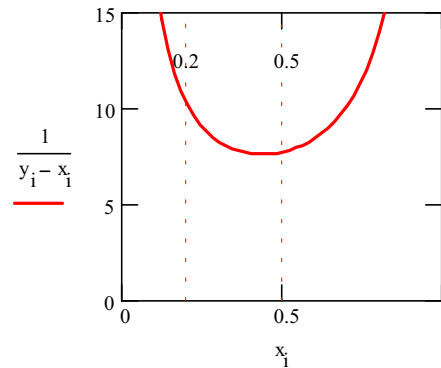
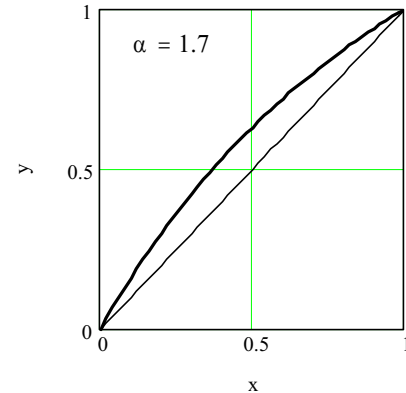
$$\int_{0.2}^{0.5} \frac{dx}{y-x} = 2.45$$

Rayleigh's equation yields

$$\frac{n(t)}{n_0} = \exp \left[- \int_{0.2}^{0.5} \frac{dx}{y-x} \right] = 0.086$$

This represents the fraction of the initial charge which remains in the still as liquid. The fraction of the initial charge which has been distilled is just unity minus this

$$1 - \frac{n(t)}{n_0} = 0.914$$

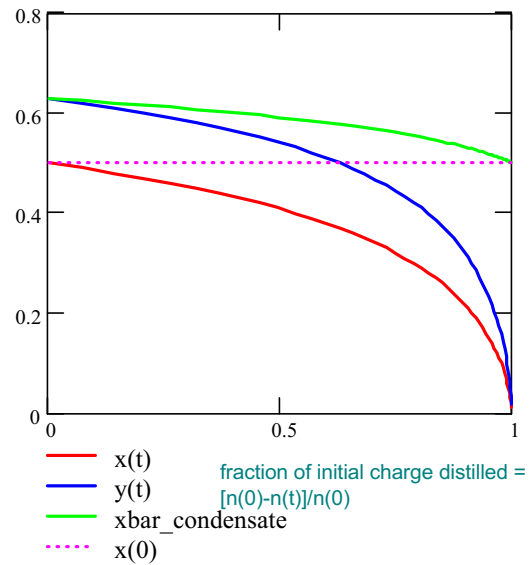


Step 4: Calculate the condensate concentration

If all the condensate is collected in a container and mixed together, the average concentration of the condensate will be

$$\begin{aligned}\bar{x}_{cond} &= \frac{\text{moles of A depleted}}{\text{total moles depleted}} \\ &= \frac{x_0 n_0 - xn}{n_0 - n} = 0.528\end{aligned}$$

The graph at right shows what typically happens as the initial liquid is more and more distilled. Notice that the vapor is initially richer than the liquid. Since the leaving vapor is richer, the remaining liquid becomes leaner. Thus both x and y become leaner as distillation proceeds.



Chapter 8. Multistage Operations

In both batch distillation and flash distillation, the separation of the two components is limited by equilibrium. For example, suppose I have a 50-50 mixture of hexane and octane. If I vaporize half of this mixture, I produce a vapor having:

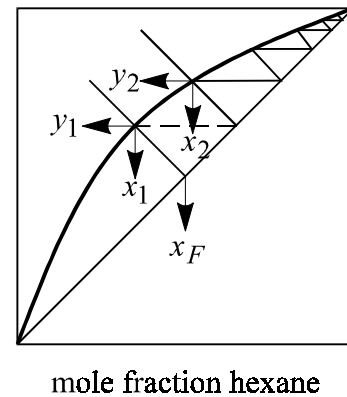
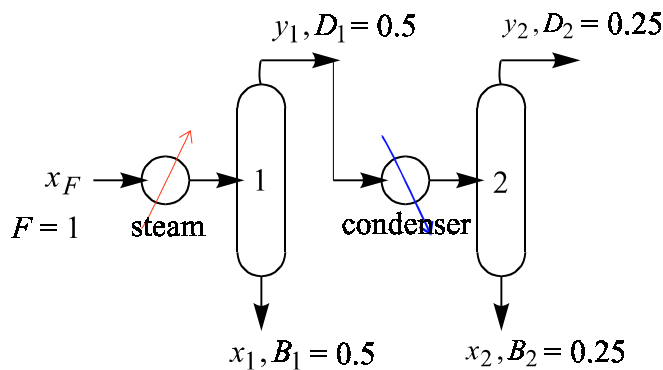
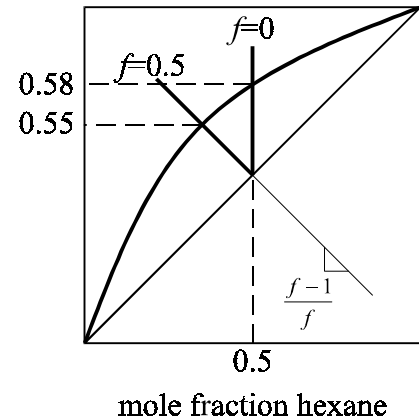
$$x_F=0.5, f=D/F=0.5 \rightarrow y_D=0.55, x_B=0.45$$

which we read off of an xy diagram. Suppose you want a 95% pure product? If I vaporized a smaller fraction of the feed, that would increase the composition of the distillate, but the best I can do is:

$$x_F=0.5, f \approx 0 \rightarrow y_D=0.58, x_B=0.5$$

This helps a little but it's still a long way from 0.95 and you don't generate much product with such a small fraction vaporized.

One solution is to take the distillate product of the first flash and partially condense it. This will produce a liquid phase which will be leaner in the more



volatile component, leaving the remaining vapor richer.

This could be repeated many times until the vapor composition reaches or exceeds the desired value. Although we have produced a stream of the desired composition, it turns out that we are "throwing out" a lot of the desired component in the "waste" streams -- the bottoms.

From the first flash unit alone, we are losing 25% of component A in the initial feed $[(1-f)x_1 \approx 0.25]$. If this component A is valuable, we don't want to throw it away.

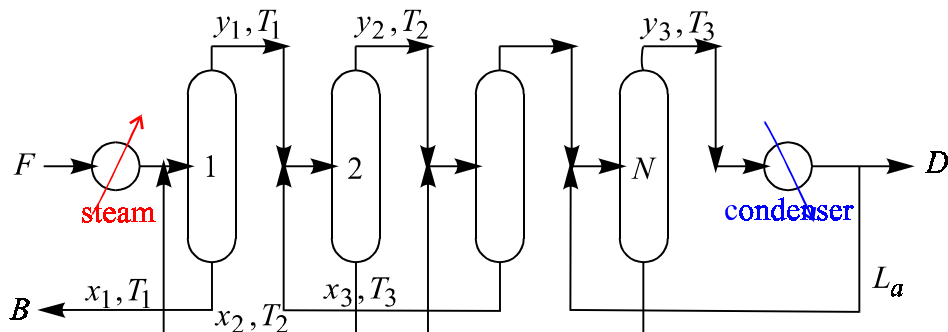
- success at achieving high y_D , but low recovery (recovery is % of A in feed which ends up on final product)

- requires $n+1$ HX'ers

Another problem is that each flash unit requires a heat exchanger and then we will need one additional heat exchanger to condense the product from the final flash unit.

COUNTER-CURRENT CASCADE

Both of these drawbacks can be removed by a slight modification: we recycle the bottoms of one flash unit into the feed of the previous flash unit.



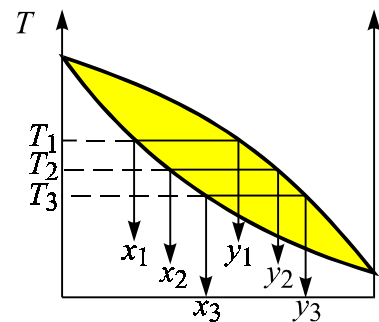
Instead of $n+1$ HXers, we now need only two. To condense the vapor, we need to transfer some of its latent heat to the liquid recycled from upstream. For this to work, the temperature of the vapor must be greater than that of the liquid. Let's see: generally, the vapor will get richer in the more volatile component as we move left to right:

$$y_1 < y_2 < \dots < y_N$$

Assuming that the vapor and liquid streams leaving each flash are in equilibrium, then the corresponding inequalities for temperature can be deduced from the typical Txy diagram at right:

$$T_1 > T_2 > \dots > T_N$$

So the recycled liquid will be cooler than the vapor it's mixed with. Thus the liquid will absorb some of the heat of the vapor. This condenses some of the vapor and vaporizes some of the liquid. Now that we have shown that the heat exchangers might be eliminated, let's return to a discussion of the countercurrent cascade.



The product recovery for a countercurrent cascade is much better than for the series of flash units without recycle. First, we have only one waste stream (B) -- instead of one from each flash. Second, the composition of this waste stream will usually turn out to be leaner in the valuable component -- because we are enriching the feed to the first flash by recycling from upstream.

Note that we also recycled some of the product liquid to condense the vapor feed to the last stage. This recycling of the product is called

reflux -- that part of the product stream recycled to the cascade

reflux ratio -- L_d/D (ratio of molar flowrates)

stage -- one unit of a cascade (e.g. one flash unit)

ideal stage -- a stage whose exit streams are at equilibrium

Chapter 9. Equipment for Tray Towers

In our schematic of a countercurrent cascade, we had the streams moving horizontally. Generally, a pump would then be required between each stage to overcome friction. With vapor and liquid, the density difference is sufficiently large, that we can use gravity to move the fluids if we stack the stages vertically rather than horizontally. A vertical stack of stages is called a *tray tower*.

At right we see a schematic of a typical *tray tower* (Treybal, p129). Each stage or flash unit is represented by one tray. Five trays are evident in Fig. 3. Liquid flows down from the tray above and flows across the tray where it comes into contact with vapor flowing upward from the tray below. After mixing, the liquid and vapor are separated, with the new liquid flow down to the tray below and the vapor flowing to the tray above. Through the act of mixing, the composition of the liquid and vapor streams has changed.

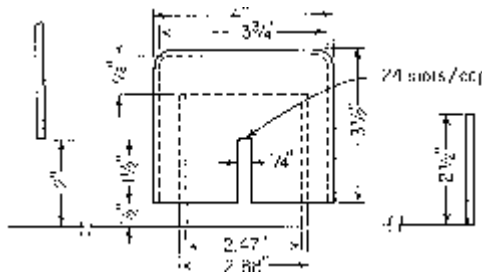


Fig. 4. An expanded view of a single "bubble cap"

The contacting of vapor and liquid on any given tray is facilitated by *bubble caps*, one of which is shown in more detail in Fig. 4. Each tray contains many bubble caps arranged in a array covering the central region of the tray (see Fig. 5).

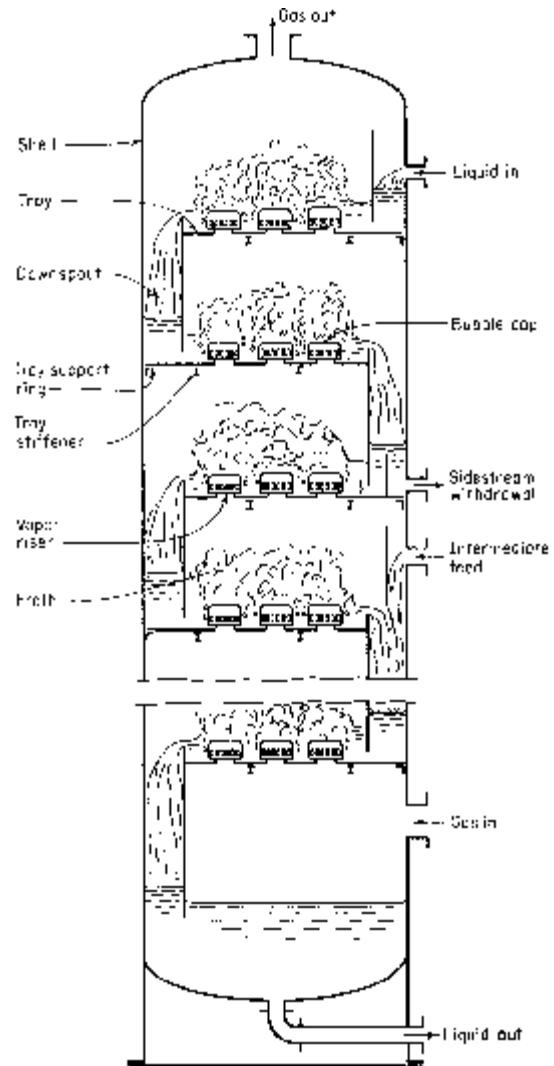


Fig. 3. A typical tray tower.

In this particular design shown in Fig. 4, vapor penetrates the tray through a circular hole 2.47 inches in diameter, upward through a 3-inch length of pipe before being diverted downward by the cap and forced through the liquid outside the pipe.

The flow pattern under both normal and abnormal operation is shown in Fig. 6.

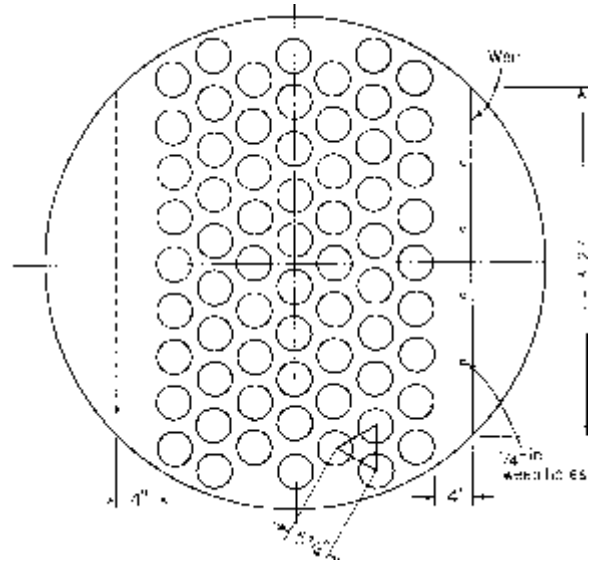


Fig. 5. Top view of arrangement of bubble caps on a tray.

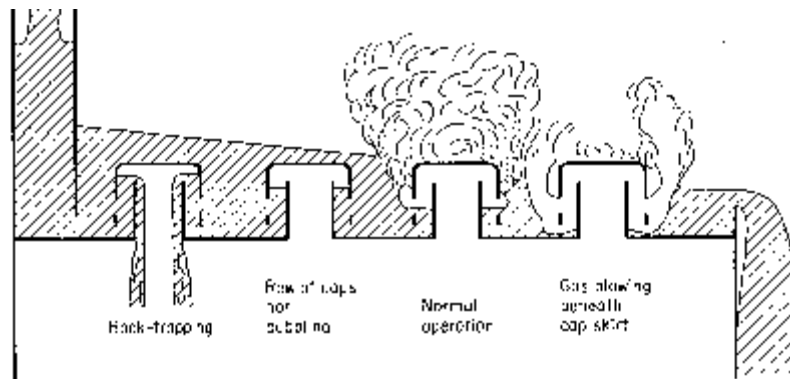


Fig. 6. Flow patterns under normal and abnormal operating of a bubble cap

An alternative tray design is the *sieve-plate* tray (see Fig. 7). Sieve-plate trays are much cheaper to fabricate compared to bubble-cap trays since the tray consists of a circular plate with holes drilled through for the passage of vapor. These holes are generally much smaller in diameter than the bubble caps.

A disadvantage of sieve plates is that they are much more prone to weeping and flooding (conditions corresponding to poor contact of liquid and vapor).

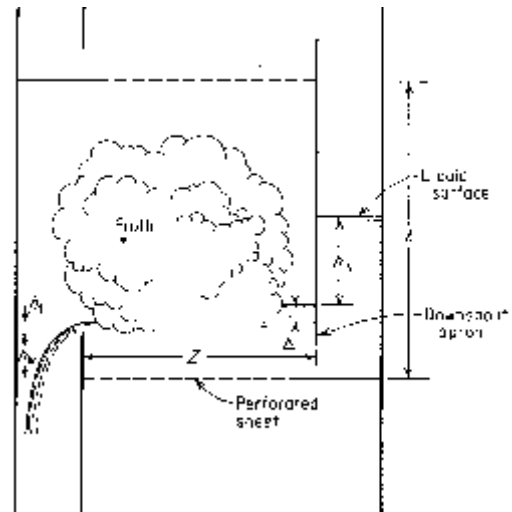


Fig. 7. Side view of a “sieve plate” tray.

Chapter 10. Performance of a C-C Cascade

ANALYSIS OF A C-C CASCADE

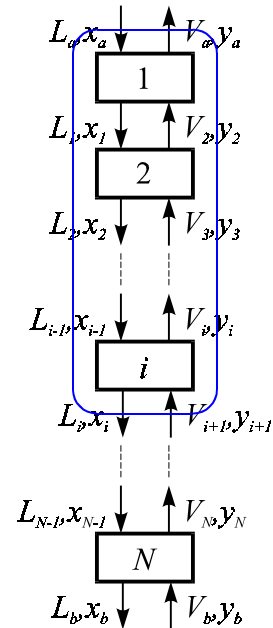
At right is a schematic representation of a countercurrent cascade. It ignores some of the details of plumbing inside the stages and, of course, in reality there are no pipes to carry the liquid and vapor between the adjacent stages. But these are unimportant details as far as mass and energy balances are concerned. The schematic preserves the essential feature -- which is that the flow of liquid and vapor occurs countercurrently.

Since we have so many streams to deal with, some convention for numbering the stages and labelling the streams will be helpful. McCabe, Smith & Harriott use the following *conventions*:

tray numbers: increase in direction of liquid flow ($1 \geq i \geq N$)

stream labels: subscripts denote stream

- L_i, V_i are **molar** flowrates of total (A+B) liquid and vapor **leaving** the i th stage.
- $L_a, V_a = V_1$ are the flowrates at the top of the cascade while L_N, V_b are the flows at the bottom of the cascade ("b" for bottom).*
- x_i, y_i are the mole fraction of the more volatile component in the liquid and vapor **leaving** the i th stage.



Suppose we know everything about the two input streams: their flowrate, composition, and enthalpy. Suppose we also have all the thermodynamic data: Hxy diagram and xy diagram.

Given: $L_a, x_a, V_b, y_b; Hxy$ and xy diagrams

We want to determine the flowrate, composition and enthalpy of the two output streams and of all the intermediate streams:

Find: L_i, x_i, V_i, y_i for $i=1, \dots, N$ ($= 4N$ unknowns)

I haven't bothered to list the enthalpies or temperatures here, because if I know the mole fraction and pressure, I can look up the enthalpy and temperature of saturated liquid or vapor.

*In heat transfer, the subscripts "a" and "b" were used for entering and leaving streams, respectively. That convention is abandoned here.

As our system, let's select the first "i" stages. An overall mole balance for this system requires:

total:
$$L_a + V_{i+1} = L_i + V_a \quad (57)$$

while a mole balance on the more volatile component requires:

component A:
$$L_a x_a + V_{i+1} y_{i+1} = L_i x_i + V_a y_a \quad (58)$$

Finally, we can also perform an enthalpy balance:

enthalpy:
$$L_a H_{x,a} + V_{i+1} H_{y,i+1} = L_i H_{x,i} + V_a H_{y,a} \quad (59)$$

Do I have enough information to calculate the result? How many independent equations do I have?

equations:
$$(57), (58), (59) \times N \quad (= 3N \text{ eqns})$$

$$x_i \text{ and } y_i \text{ at equil.} \quad (= N \text{ eqns})$$

So, at least when I am dealing with *ideal stages*, I have as many equations as unknowns.

Many distillation towers have $N=20$ stages or more, so I could easily be talking about 80 equations -- a formidable problem. Fortunately, there are assumptions which can make this problem tractable so that it can be solved easily with pencil and paper.

CONSTANT MOLAL OVERFLOW

In our discussion of flash distillation, we noted that many pure components have the same heat of vaporization per mole. If you can assume that the molar heat of vaporization of the mixture is completely independent of its composition, then solution is greatly simplified.

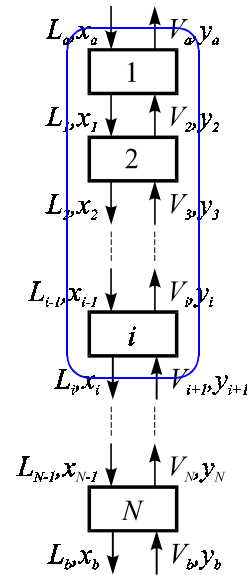
Assumptions:

- 1) $H_{y,i} - H_{x,i} = \lambda$ for all i .
- 2) neglect sensible heat compared to latent heat

Let's choose saturated liquid having the composition of the feed as our reference state for enthalpies. Since the only difference between the various liquid streams is sensible heat, we take them all to be equal -- equal to zero:

$$H_{x,a} = H_{x,i} = 0 \quad \text{for all } i$$

and
$$H_{y,i+1} = H_{y,a} = \lambda$$



With these assumptions, the enthalpy balance about the top i stages

$$L_a H_{x,a} + V_{i+1} H_{y,i+1} = L_i H_{x,i} + V_a H_{y,a} \quad (60)$$

simplifies to:

$$V_{i+1} = V_a \text{ for all } i \quad (61)$$

and the total mole balance about the top i stages

$$L_a + V_{i+1} = L_i + V_a \quad (62)$$

Subtracting (16) from (15):

$$L_a = L_i \text{ for all } i$$

In other words, all of the vapor streams have the same **molar** flowrate within the cascade (although their composition and mass flowrate will change) and all the liquid streams have the same molar flowrate:

$$V_a = V_1 = V_2 = \dots = V_N = V_b (= V, \text{ say})$$

$$L_a = L_1 = L_2 = \dots = L_N = L_b (= L, \text{ say})$$

which is called the state of **constant molar overflow**. Since the input flowrates are known, we know all the flowrates. Thus we have just halved the number of unknowns from $4N$ to $2N$. We can then drop the subscripts on the flowrates and forget the enthalpy balance (60) and the total mole balance (62). This leaves just the component mole balance

$$L_a x_a + V_{i+1} y_{i+1} = L_i x_i + V_a y_a$$

which can be rearranged to:
$$y_{i+1} = \frac{L}{V} x_i + \left(y_a - \frac{L}{V} x_a \right) \quad (63)$$

or

$$y_{i+1} = m x_i + b$$

which is a straight line on an xy diagram. This line is called the:

operating line — y_{i+1} vs. x_i ; a graphical representation of the mass balance.

Another important curve on an xy diagram is the:

equilibrium curve — y_i vs. x_i ; a graphical representation of VLE

In the next section, we will see how these two curves can be used to determine the number of equilibrium stages required to achieve some desired degree of separation.

A RECTIFYING CASCADE

In a typical distillation tower, the liquid fed to the top of the enriching cascade is a portion of the vapor product which has been condensed and refluxed back into the tower, as shown at right. The ratio of the amount refluxed to the amount not refluxed is called the *reflux ratio*

$$R \equiv \frac{L}{D} \quad (64)$$

Since all of the vapor stream leaving the top of the cascade is condensed to form the distillate product and the liquid fed to the top, the three streams must have the same composition:

$$x_D = x_a = y_a \quad (65)$$

Then the operating line (63) can be simplified to[♠]

$$y_{i+1} = \frac{L}{V} x_i + \underbrace{\left(1 - \frac{L}{V}\right)}_{\frac{V-L}{V} = \frac{D}{V}} x_D = \frac{L}{V} x_i + \frac{D}{V} x_D \quad (66)$$

The ratio of the flowrates can be expressed in terms of the reflux ratio R using (64):

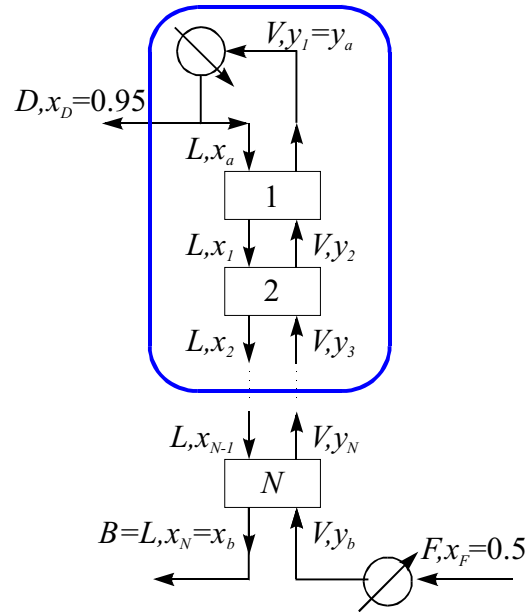
$$\frac{L}{V} = \frac{L}{L+D} = \frac{RD}{RD+D} = \frac{R}{R+1} \quad (67)$$

$$\frac{D}{V} = \frac{D}{L+D} = \frac{D}{RD+D} = \frac{1}{R+1}$$

The operating line (66) can be rewritten as

$$y_{i+1} = \frac{R}{R+1} x_i + \frac{1}{R+1} x_D \quad (68)$$

Thus the slope of the operating line (a plot of y_{i+1} versus x_i) is $R/(R+1)$.



[♠] Alternatively, we could “start over” and perform a component mole balance on the top i stages of the cascade (indicated by the blue line in the sketch).

Now, one point on the operating line is $x_i = y_{i+1} = x_D$. In other words, if we substitute x_D for both x_i and y_{i+1} , (68) is automatically satisfied.

Example. Suppose I have a feed stream containing 50% alcohol in water which I want to enrich to 95% alcohol. How many stages do I need if I use a reflux ratio of unity and what will be the flowrate of this product?

Given: x_F, x_D, F and R

Find: N and D

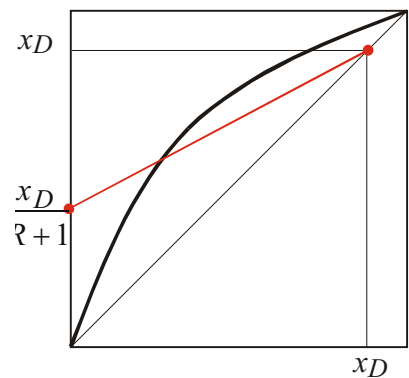
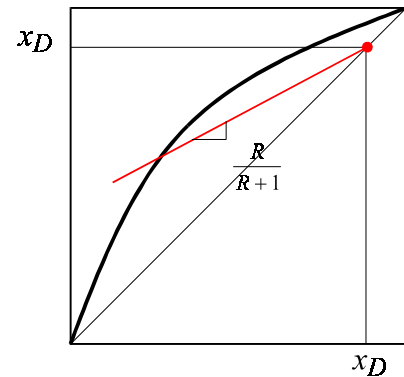
Solution: The first step is to draw the operating line on the xy -diagram. One point is (x_D, x_D) or $(0.95, 0.95)$. And the slope is $R/(R+1) = 1/2$ for $R=1$. Armed with one point and the slope, we could draw the line. But it is usually easier to construct a line if we know two points. A second convenient point corresponds to the y -intercept. Substituting $x_i = 0$ into (68) yields

$$x_i = 0: \quad y_{i+1} = \frac{x_D}{R+1}$$

which can be conveniently calculated from what's given. Thus $\left(0, \frac{x_D}{R+1}\right)$ is a second point on our operating line. Knowing the slope and one point, or two points, we can draw the operating line.* Once the operating line is plotted on the xy diagram (which is the equilibrium curve), we can determine the composition of other streams as follows.

The two streams leaving a given *ideal* stage are at equilibrium, thus ***the compositions of the two streams leaving a given stage must lie on the equil. curve.*** Since we already know the composition of the vapor stream leaving stage 1 ($y_1 = x_D = 0.95$), we can determine x_1 by moving horizontally from one point on the operating line (x_D, x_D) to one point on the equilibrium curve and then read off the value of x_1 :

(x_1, y_1) on equil. curve: gives x_1

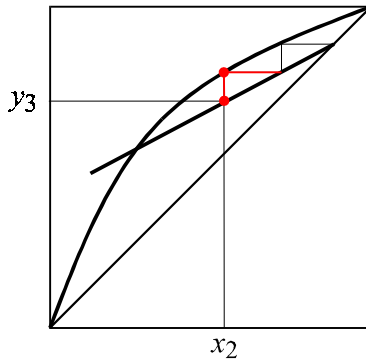
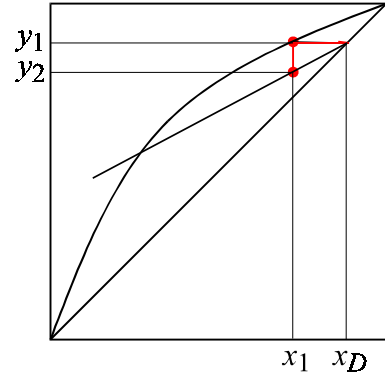


* The point (x_D, x_D) and slope of $1/2$ are not drawn to scale in the sketches. For that matter, neither is the equilibrium curve. However, given the equilibrium curve and operating line as drawn, the method of stepping off the number of stages is correct.

On the other hand, the operating line represents a component mole balance about an arbitrary number of stages measured from the top. In particular, for just the top stage, the operating line (66) gives me a relationship between x_1 and y_2 :

(x_1, y_2) on oper. line: gives y_2

Knowing x_1 , I can determine y_2 . In general, **the compositions of the two streams between a given pair of adjacent stages must lie on the operating line.** Now I can repeat the process:



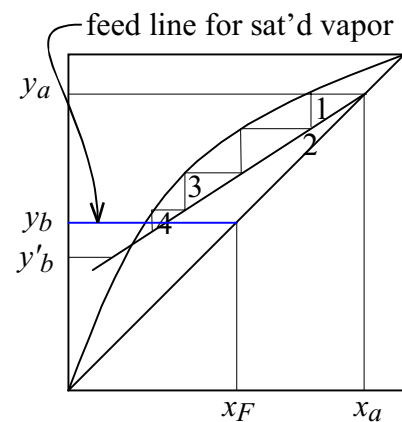
(x_2, y_2) on equil. curve: gives x_2

(x_2, y_3) on oper. line: gives y_3

and so on. Continuing to step off stages in this manner until the vapor mole fraction equals or drops below $x_F = y_b$, requires four steps:

answer: $N = 4$

Comment #1: Although the feed might be a liquid, it's the vapor mole fraction which must be at or below the feed composition, because the actual feed to be bottom of the cascade is a vapor (see stream whose composition is labelled y_b in the flowsheet on page 73). The horizontal line $y = x_F (= y_b)$ on the xy -diagram is called the **feed line**.



Comment #2: After taking 4 steps (or any integer number), we don't end up exactly at the feed composition (except by some extreme stroke of luck). Instead we end up stepping below the feed composition. If the trays really are perfectly ideal, and the feed composition is 0.5, the distillate composition would turn out to be slightly richer than 0.95. Although any real column has an integer number of trays, it is customary to report the answer as a fraction; for example, to go from a feed of 0.50 to a distillate of 0.95, we require 3.7 ideal stages (or $3 + 0.7$, where 0.7 is the fraction of the last step which corresponds to the feed composition) in the current problem.

Comment #3: Suppose that our feed composition had been a little lower, say y'_b . No matter how many steps we took, we could never get a vapor composition lower than that at the intersection of the operating and equilibrium curves. In that case, any solution for the specified reflux ratio is impossible. Instead the reflux ratio would have to be increased, which will rotate the operating line counter-clockwise about the specified point. This will lower the composition at the intersection point and make the separation possible. It turns out there exists a minimum value of

the reflux ratio which allows a particular distillate composition x_D to be produced from a given feed composition x_F . This called the *minimum reflux ratio*.

Let's finish this problem by calculating the flowrates. Since the vapor flowrate leaving each tray is the same, and because we are creating the vapor to the first tray by completely vaporizing the feed, we can say that

$$V = F$$

The ratio of liquid to vapor flowrate inside the cascade is given in terms of the known reflux ratio by (67):

$$\frac{L}{V} = \frac{R}{R+1} \stackrel{R=1}{=} \frac{1}{2} \quad \text{or} \quad L = \frac{1}{2}V = \frac{1}{2}F$$

Since the bottoms stream B is one of the liquid streams

$$B = L = \frac{1}{2}F$$

Finally, the distillate flowrate can be calculated from the definition of the reflux ratio: recall (64):

$$D = \frac{L}{R} \stackrel{R=1}{=} L = \frac{1}{2}F$$

A STRIPPING CASCADE

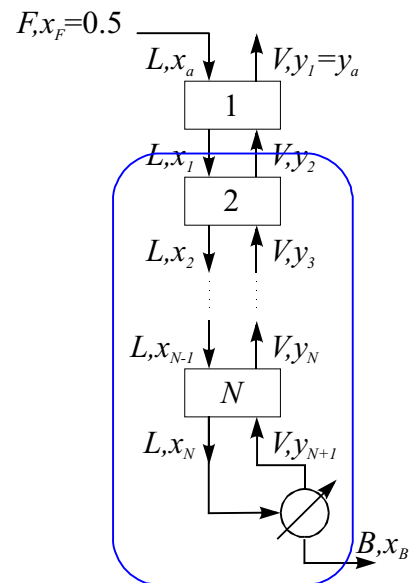
Use of a single cascade with 3.7 stages allows us to convert a feed of 50mol% alcohol into one containing 95mol%. But a significant amount of the alcohol is being lost in the second product stream. It's possible to strip the alcohol from this stream by feeding it to a second cascade.

In a stripping cascade, liquid is fed into the top. Liquid out the bottom of the cascade is partially vaporized and the vapor is recycled into the bottom of the cascade. The vapor stream at the top represents the second product stream.

Because the bottoms product is only partially vaporized to form the vapor stream which is recycled to the cascade, its composition is not the same as the bottoms product. In other words

$$x_N \neq y_{N+1} \neq x_B$$

So no analogy can be made to (65). However we still have a



operating-line relationship like (63) or (66) which is imposed by mole balances. From a balance over the entire stripping cascade on the more volatile component, we know that

$$\underbrace{Lx_a = Fx_F}_{\text{in}} = \underbrace{Bx_B + Vy_a}_{\text{out}}$$

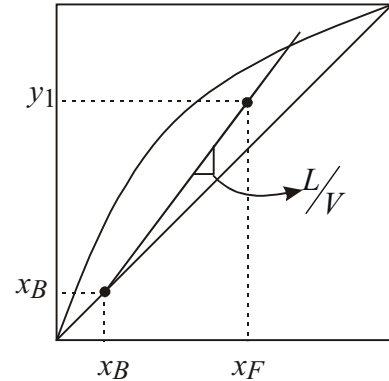
so

$$Vy_a - Lx_a = -Bx_B$$

Substituting this result into (63), the operating line for a stripping cascade becomes[♠]

$$y_{i+1} = \frac{L}{V}x_i - \frac{B}{V}x_B \quad (69)$$

Like all the operating lines we've encountered so far, this one has a slope of L/V . One point on this operating line is (x_B, x_B) since substituting $y_{i+1} = x_i = x_B$ automatically satisfies (69) provided $L - B = V$ which is always true since this represents a total mole balance. Another point is (x_F, y_1) if we happen to know or can somehow calculate y_1 . Then we have two points and can draw the operating line. Otherwise, we use one point and the slope.



Example. Suppose I have a feed stream containing 50% alcohol in water which I want to strip the alcohol from to produce a stream containing only 5% alcohol. How many stages do I need if I boil half of the liquid leaving the bottom of the cascade and return it as vapor?

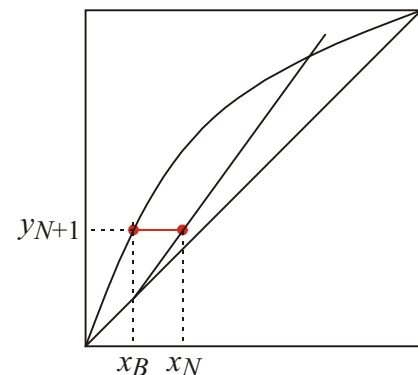
Given: x_F, x_B and V/L

Find: N

Solution: Once again, vapor and liquid streams leaving the same stage are assumed to be at equilibrium; thus (x_i, y_i) lies on the equilibrium curve. On the other hand, the composition of adjacent streams (x_i, y_{i+1}) lies on an operating line for this cascade. One point on this operating line is $x_i = y_{i+1} = x_B$. If we “boil half the liquid leaving the bottom of the cascade and return it as vapor” we know that $V = L/2$, so the slope of the operating line is:

$$L/V = 2$$

Knowing the slope and one point, we can immediately draw



[♠] Alternatively, we could “start over” and perform a component mole balance on the bottom $N-i$ stages of the cascade (indicated by the blue line in the sketch).

the operating line. The liquid product being drawn off at x_B is in equilibrium with the vapor being sent back into the cascade; thus (x_B, y_{N+1}) lies on the equilibrium curve. On the other hand, (x_N, y_{N+1}) are adjacent streams in the cascade and so their compositions must lie on the operating line.

Similarly, (x_N, y_N) lies on the equilibrium curve, while (x_{N-1}, y_N) lies on the operating line.

We continue to step off stages in this manner until we step past a liquid composition equal to the feed x_F ; in other words, we continue stepping until we cross the blue vertical feed line. In this case, three steps are required. But one of these steps is the reboiler; only two additional equilibrium trays are required:

answer: $N=2$ plus reboiler

Comment #1: Notice that the “feed line” for a stripping cascade is vertical, whereas the feed line for a rectifying cascade was horizontal (see page 75). This is because the feed into the bottom of a rectifying cascade is a vapor, whereas the feed to a stripping cascade is a liquid.

Comment #2: Suppose that our feed composition had been a little higher, say x_F' . No matter how many steps we took, we could never get a liquid composition higher than that at the intersection of the operating and equilibrium curves. In that case, any solution for the specified L/V ratio is impossible. Instead the L/V ratio would have to be decreased, which will rotate the operating line clockwise about the specified point. This will raise the liquid composition at the intersection point and make the separation possible. It turns out there exists maximum L/V , or a minimum vapor rate V which allows a particular bottoms composition x_B to be produced from a given feed composition x_F and liquid flowrate L . This minimum V/L is called the **minimum boil-up ratio**.

Let's finish the problem by determining the flowrates. Once again, all the flowrates can be deduced from the equimolal overflow assumption and the reboil fraction. All the liquid flowrates correspond to the flowrate of the liquid fed to the top:

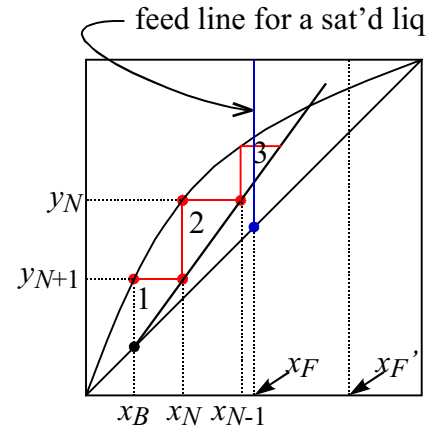
$$L = F$$

Since I'm reboiling half of this liquid to return to the cascade as vapor, all the vapor flowrates are

$$V = L/2 = F/2$$

The bottoms flowrate is what remains after half of the liquid to the reboiler is boiled:

$$B = L - V = F/2$$



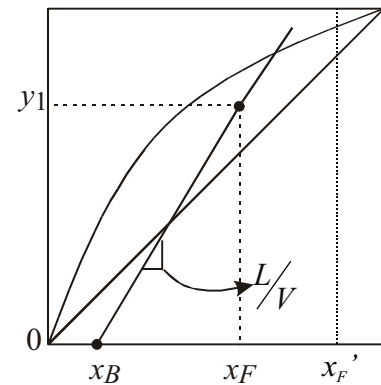
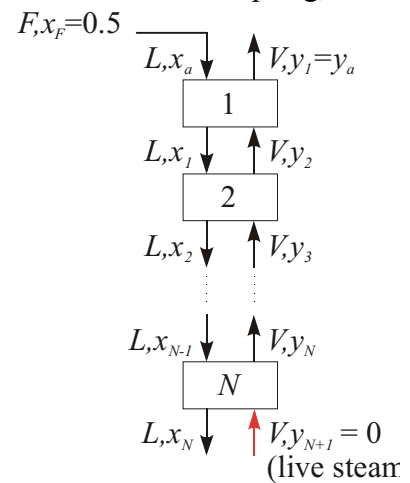
STEAM DISTILLATION

Instead of using a heat exchanger to partially boil the liquid stream leaving the bottom stage to produce the vapor entering the bottom stage, we could directly inject steam as the vapor. This has the advantage that it avoids the cost of a heat exchanger and you are getting direct contact between the hot and cold fluids.

Of course, use of steam as the vapor is only useful if water is one of the two components being separated (e.g. alcohol/water) and further, it must be the less volatile component. If instead you are trying to separate heptane from octane, injecting steam would produce a second liquid phase (since oil and water are not miscible).

This produces the operating line shown at right. Note that one point on the operating line is $(x_B, 0)$ since the “vapor” entering the bottom is pure steam (water). Of course, part of the operating line lies below the 45° line ($x=y$). But there are no restrictions that y must be larger than x . As with the stripping cascade, we continue to step off stages between the operating line and the equilibrium curve until our liquid composition exceeds x_F .

Comment: Suppose that our feed composition had been a little higher, say x_F' . No matter how many steps we took, we could never get a liquid composition higher than that at the intersection of the operating and equilibrium curves. In that case, any solution for the specified L/V ratio is impossible. Instead the L/V ratio would have to be decreased, which will rotate the operating line clockwise about the specified point. This will raise the composition at the intersection point and make the separation possible. It turns out there exists maximum L/V , or a minimum steam rate V which allows a particular bottoms composition x_B to be produced from a given feed composition x_F and liquid flowrate L .



Chapter 11. McCabe-Thiele Method

A typical distillation tower will consist of at least two cascades -- one to enrich the feed in the more volatile component and a second one to strip the more volatile component out of the bottoms stream before disposing of it.

rectification -- enrichment of vapor by contact with liquid reflux

With enough trays, we can usually make D as pure as we like (an exception occurs for an azeotropic mixture). However, the liquid stream at the bottom of the cascade might still contain a significant fraction of the more volatile component. This is where a second cascade is useful:

stripping -- removal of the more volatile component from a liquid by contact with reboiled bottoms (or direct injection of steam)

A typical problem in designing a distillation column is the following:

Given: $z_F, x_D, x_B, L/D, H_F$

Find: N and \bar{N}

where N and \bar{N} are the number of stages in enriching and stripping sections. Having two cascades is a little trickier than one, so let me first tell you how to solve the problem by giving you the recipe, and later we will rationalize some of the steps in this recipe.

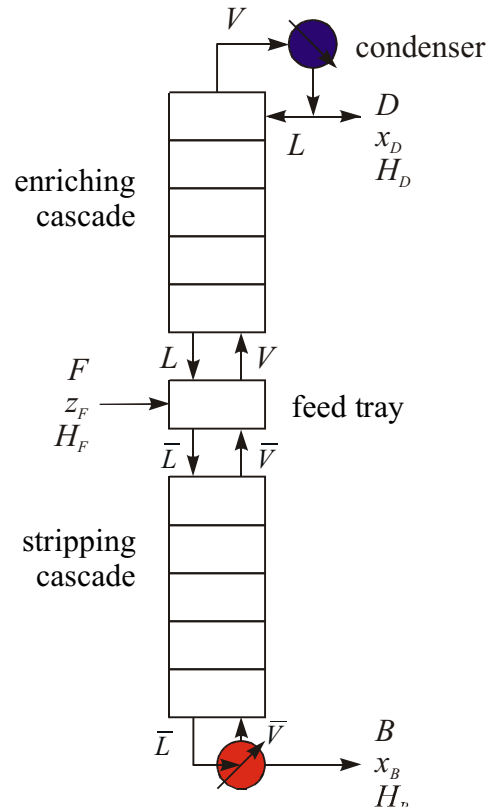
This recipe is called the **MCCabe-Thiele Method** and it works when you have only two components and you can assume equal molal overflow.

Step 1) Plot equilibrium data on an xy diagram.

Step 2) Locate x_B, z_F , and x_D on 45° line

We use " z_F " to denote the mole fraction ignoring which phase the feed is in:

$$z_F \equiv \frac{\text{moles of A in liquid} + \text{vapor}}{\text{total moles in liquid} + \text{vapor}}$$



Step 3) Calculate q (a dimensionless variable representing the thermal condition of the feed):

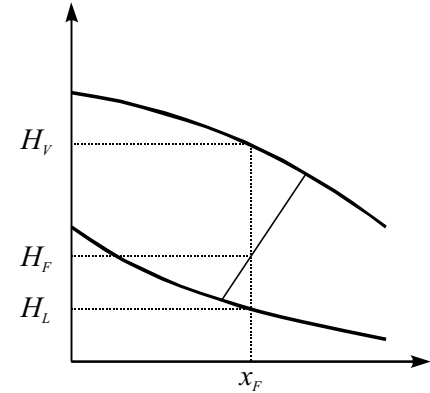
$$q \equiv \frac{H_V - H_F}{H_V - H_L}$$

where

H_F = enthalpy of feed

H_V = H of sat'd vapor with $y=z_F$

H_L = H of sat'd liq. with $x=z_F$



Step 4) Plot q -line, which is a line given by the following equation (Q.L.):

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

Of course, the name " q -line" is given because this line depends on q — the thermal condition of the feed. For example, suppose the feed is ...

superheated vapor:

$$H_F > H_V \rightarrow q < 0 \rightarrow 0 < \frac{q}{q-1} < 1$$

sat'd vapor:

$$H_F = H_V \rightarrow q = 0 \rightarrow \frac{q}{q-1} = 0 \text{ (horizontal line)}$$

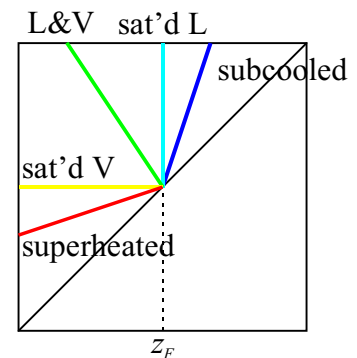
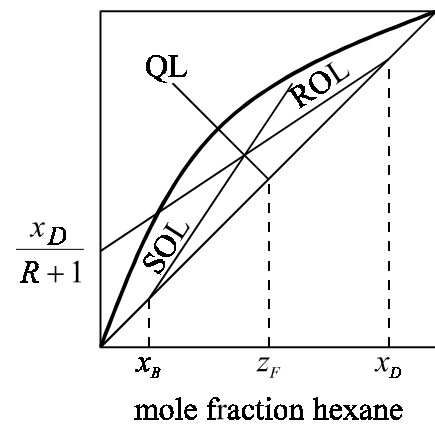
2-phases mixture: $H_L < H_F < H_V \rightarrow 0 < q < 1 \rightarrow \frac{q}{q-1} < 0$

In this case, q represents the fraction of the feed which is liquid.

sat'd liquid: $H_F = H_L \rightarrow q = 1 \rightarrow \frac{q}{q-1} = \infty$ (vertical line)

subcooled liquid: $H_F < H_L \rightarrow q > 1 \rightarrow 1 < \frac{q}{q-1} < +\infty$

As it turns out, the two operating lines for the two cascades intersect somewhere along this line.



one point: (z_F, z_F)

slope: $q/(q-1)$

Step 5) Plot the operating line for the rectification section (R.O.L.):

$$y = \frac{R}{R+1}x + \frac{x_D}{R+1}$$

one point: (x_D, x_D)

another point: $(0, x_D/(R+1))$

Step 6) Plot the operating line for the stripping section (S.O.L.):

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

one point: (x_B, x_B)

another point: intersection of R.O.L. and Q.L.

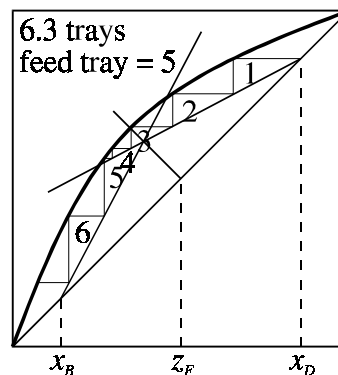
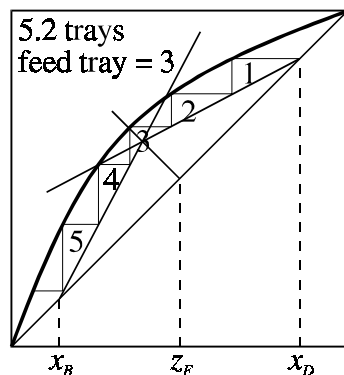
Step 7) Step off stages

You could start at either end ($x=y=x_D$ or $x=y=x_B$), although it is customary to start at the top. In stepping off the stages, you eventually have a choice as to which operating line to drop down to.

LOCATION OF FEED PLATE

At some point during the stepping process, you will have a choice of either operating line to step down to. Either operating line can be used, but once you switch operating lines, you cannot go back to the original line: switching operating lines corresponds to switching from one cascade to the other. The stage at which we switch operating lines is the

feed plate: stage at which you switch operating lines



Either of the two stepping schemes above is OK, but one scheme leads to fewer total trays than the other.

optimum feed plate: to get the fewest number of total stages, you switch operating lines when that allows you to take larger steps

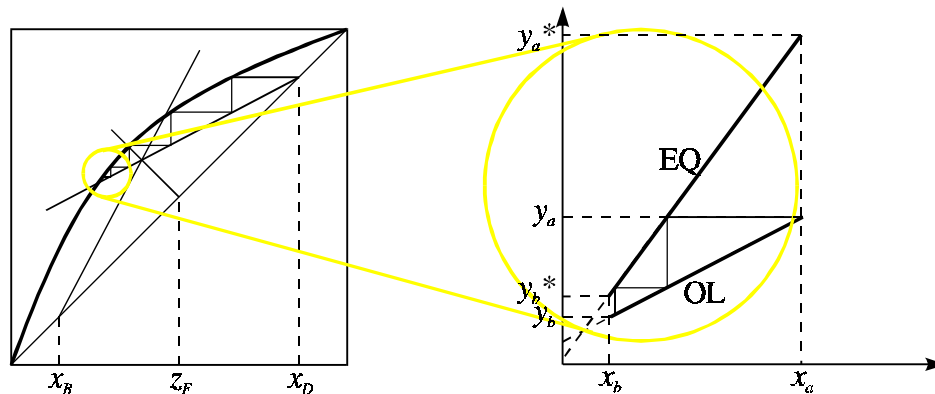
In other words, if you have a choice of which operating line to use, use that one which takes you furthest from the equilibrium curve. This choice gives the biggest step and fewest total stages.

CONVERGENCE OF OPERATING LINE AND EQUILIBRIUM CURVE

In some of the homework problems, the distance between the operating line and equilibrium curve becomes very small near the point of their intersection. When this happens, a very large number of steps might be required to make any progress on separation.

Rule: an *infinite* number of steps is required to get to an intersection of the operating line and equilibrium curve.

Proof: when the size of your steps are no longer large compared to the width of the pen or pencil you are using to draw them, you should "blow up" the drawing to reduce drawing errors.

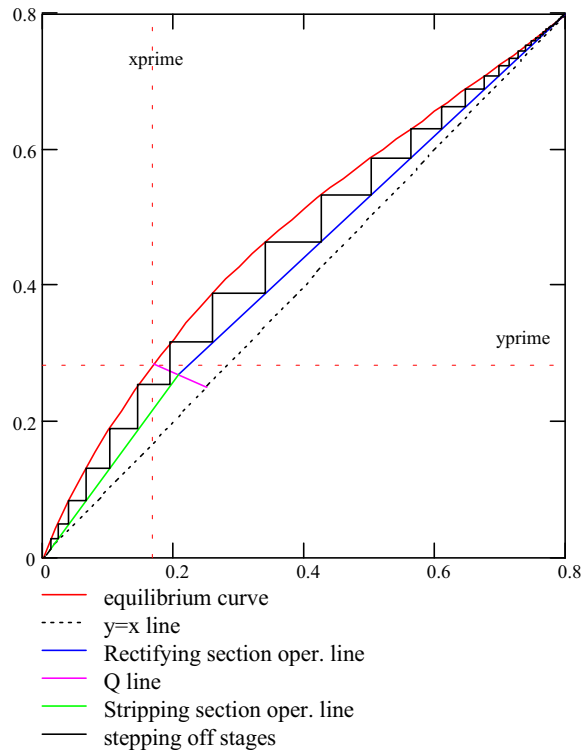


To demonstrate this graphically, let me present the results of stepping off stages in a particular example:

Example: given the xy-diagram for ethanol and water at 1 atm pressure (has an azeotrope at $x = y = 0.8$), step off stages for the following conditions:

Given: $z_F = 0.25$, $x_D = 0.7999$, $x_B = 0.01$, $q = 0.3$

Find: N and \bar{N} for the optimum feed location



Enter values:

$\eta = 1$	Murphree plate efficiency	
$x_D = 0.7999$	Mol frac in distillate	
$x_F = 0.25$	Mol frac in feed	
$x_B = 0.01$	Mol frac in bottoms	
$q = 0.3$	Thermal conditions of feed (liquid fraction)	
$R = 8.618$	Reflux ratio (to obtain total reflux, use $R=0$)	$R_{min} = 4.483$

After N steps, this is actual x_B

$$x_{B_{calc}} = 5.57 \cdot 10^{-3}$$

Nrect = 60 Feed tray

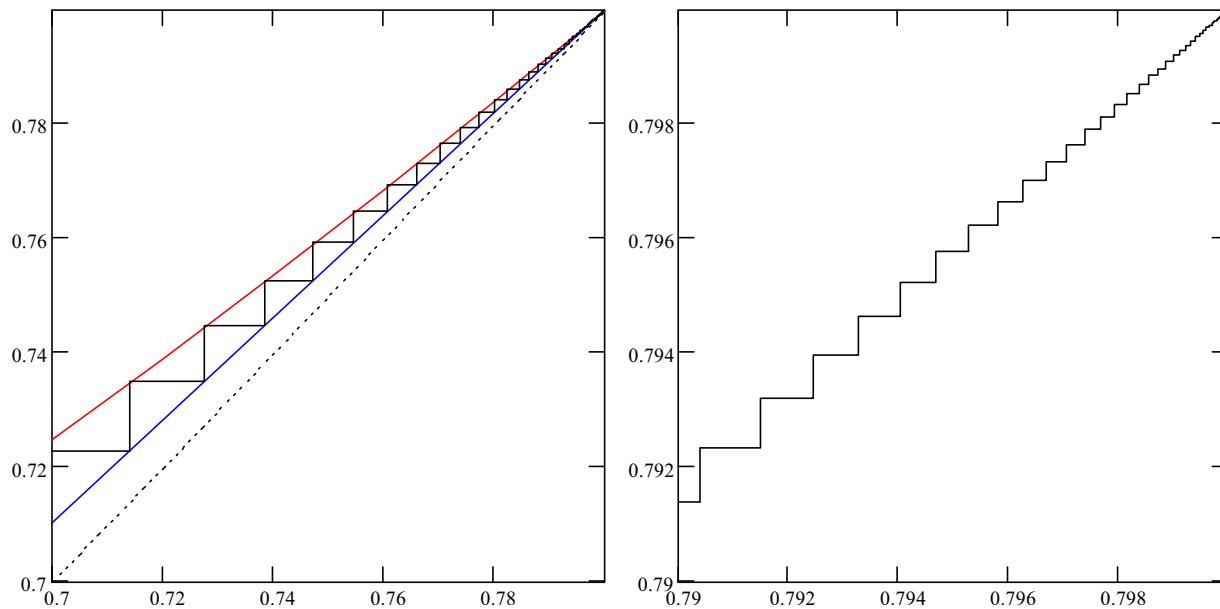
N = 67 Total number of stages

Solution: This is a particularly difficult separation because the distillation composition $x_D = 0.7999$ is very close to the azeotrope. We anticipate a large number of steps. Available online is a Mathcad document [McCabe-Thiele (Pro).mcd] which steps off stages automatically using the optimum feed location.

The results are shown in the figure at right. The program reports (not shown) the total number of steps and the feed location. In this figure, there are a total of 67 steps with the feed introduced on the 60th from the top. In the upper right corner, the steps are becoming so small as to be invisible.

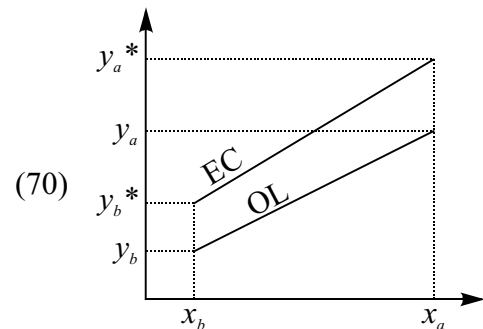
The below on the left is a blow-up of the region from 0.7 to 0.8. Even on this blow-up the steps are becoming invisible in the upper right corner. So the second graph below on the right is another blow-up: this from 0.79 to 0.80. Still the steps are becoming vanishingly small.

The red (equilibrium) curve does not show up on the second graph below on the right. However, the equilibrium curve is just the locus of points from the upper-left corner of each step. Similarly, the lower right corner of each step is the operating line. Notice that in these blow-ups, both the equilibrium curve and the operating line very linear.



Over a narrow range, any continuous curve becomes virtually linear. When both the operating line and equilibrium curve are straight lines, an analytic expression exists for calculating the number of steps:

$$N = \frac{\log \left[\frac{(y_a^* - y_a) / (y_b^* - y_b)}{(y_a^* - y_b^*) / (y_a - y_b)} \right]}{\log \left[\frac{(y_a^* - y_b^*) / (y_a - y_b)}{(y_a^* - y_b^*) / (y_a - y_b)} \right]}$$



which is called **Kremser's equation**. The subscripts a and b denote streams at the top and bottom of the cascade, respectively; the y^* are vapor compositions in equilibrium with the liquid at the top and bottom of the cascade.

Proof: the linear equilibrium curve can be expressed as

$$y_i = mx_i + b \quad (71)$$

A mole balance about the top i stages of the cascade yields

$$y_{i+1} = \frac{L}{V} x_i + \left(y_a - \frac{L}{V} x_a \right)$$

Using (71) to eliminate x_i :

$$y_{i+1} = \frac{L}{V} \frac{y_i - b}{m} + \left(y_a - \frac{L}{V} x_a \right)$$

Now we define a new parameter, which represents the ratio of the slope of the operating line (L/V) to the slope of the equilibrium curve (m):

$$A \equiv \frac{L}{mV}$$

In terms of A , our mole balance becomes

$$y_{i+1} = A(y_i - b) + y_a - Amx_a = Ay_i + y_a - A \underbrace{(mx_a + b)}_{y_a^*}$$

From (71), we see that $mx_a + b$ is just the vapor concentration in equilibrium with liquid at concentration x_a , which we denote at y_a^* . After minor rearrangement, the above equation becomes

$$y_{i+1} = Ay_i - Ay_a^* + y_a \quad (72)$$

This serves as a recursion formula, which we can applied repeatedly to obtain the concentration on successive stages, starting at the top. For $i=1$, recalling $y_1 = y_a$, (72) yields

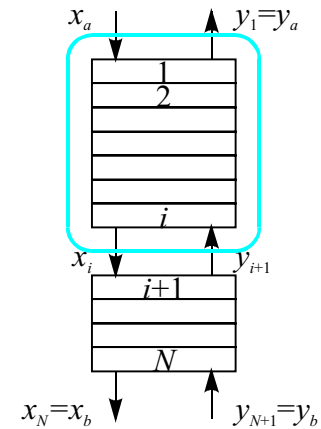
$$i = 1: \quad y_2 = A \underbrace{y_1}_{y_a} - Ay_a^* + y_a = y_a (1 + A) - Ay_a^*$$

$$i = 2: \quad y_3 = Ay_2 - Ay_a^* + y_a = A[y_a (1 + A) - Ay_a^*] - Ay_a^* + y_a \\ = y_a (1 + A + A^2) - y_a^* (A + A^2)$$

where the second equality above results from substituting y_2 from the previous step. Now we begin to see a pattern developing:

$$i = n: \quad y_{n+1} = y_a (1 + A + A^2 + \dots + A^n) - y_a^* (A + A^2 + \dots + A^n) \quad (73)$$

The sums represent partial sums of geometric series, whose sum is known analytically:



$$1 + A + A^2 + \dots + A^n = \frac{1 - A^{n+1}}{1 - A}$$

Substituting this result into (73):

$$y_{n+1} = y_a \frac{1 - A^{n+1}}{1 - A} - y_a^* A \frac{1 - A^n}{1 - A}$$

For the bottom stage of the cascade, $n=N$ and $y_{N+1} = y_b$:

$$y_b = y_a \frac{1 - A^{N+1}}{1 - A} - y_a^* A \frac{1 - A^N}{1 - A}$$

Multiplying through by $1-A$ and collecting terms multiplied by A or by A^{N+1} :

$$y_b - y_a + A(y_a^* - y_b) = A^{N+1}(y_a^* - y_a) \quad (74)$$

This can be simplified. Recall that A is defined as the ratio of the slopes of the operating line to the equilibrium curve. This ratio can be calculated from the concentration defined on the xy-diagram above:

$$A \equiv \frac{\text{slope of OL}}{\text{slope of EC}} = \frac{(y_a - y_b) / (x_a - x_b)}{(y_a^* - y_b^*) / (x_a - x_b)} = \frac{y_a - y_b}{y_a^* - y_b^*} \quad (75)$$

We can use this result to obtain $y_a - y_b = A(y_a^* - y_b^*)$, which will now be substituted into (74):

$$\underbrace{A(y_b^* - y_a^*) + A(y_a^* - y_b)}_{A(y_b^* - y_a^* + y_a^* - y_b) = A(y_b^* - y_b^*)} = A^{N+1}(y_a^* - y_a)$$

After dividing through by A and solving for A^N :

$$A^N = \frac{y_b^* - y_b}{y_a^* - y_a} \quad \text{or} \quad N = \frac{\log\left(\frac{y_b^* - y_b}{y_a^* - y_a}\right)}{\log A}$$

Taking the log of both sides, recalling that $\log(A^N) = N \log A$, then solving for N we obtain the second expression above. To obtain the form of Kremser's equation given as (70), we substitute (75) for A .

Comment #1: In the xy-diagram shown next to (70), the equilibrium curve lies above the operating line. In other words, $y_a^* > y_a$ and $y_b^* > y_b$. To obtain $N > 0$, you must have $y_a > y_b$. If

you inadvertently (but consistently) interchange the subscripts a and b , you will obtain negative values for N . Kremser's equation can also be applied to situations in which the operating line lies above the equilibrium curve; then to obtain $N > 0$, the inequalities above must be reversed.

Comment #2: If the operating line and equilibrium curve should cross (which is physically impossible), when evaluating (70) you will find yourself trying evaluate the log of a negative number.

Comment #3: The situation in which the operating line and equilibrium curve are parallel (i.e. $A = 1$) is a special case: (70) becomes indeterminate. However, since the driving force $y^* - y$ is constant, the number of steps is just the total change in concentration divided by the driving force:

for $A = 1$:

$$N = \frac{y_a - y_b}{y_a^* - y_b^*}$$

Now we will return to discuss the motivation for Kremser's equation: approaching the intersection of OL and EC:

Notice that, as x_b approaches the point of intersection (see figure on p83), $y_b^* \rightarrow y_b$ and

$$N = \frac{\log\left[\frac{()}{0}\right]}{\log[]} = \frac{\log[\infty]}{\log[]} \rightarrow \infty$$

Thus *you can never reach the point of intersection* for any finite number of steps. In particular, a very large number of stages is required as we increase the purity of either of our two product streams. For example, as $x_D \rightarrow 1$, the end-point (x_D, x_D) of our operating line approaches $(1,1)$, which is always one point on the equilibrium curve: as $x_D \rightarrow 1$, $N \rightarrow \infty$.

CHOOSING THE REFLUX RATIO

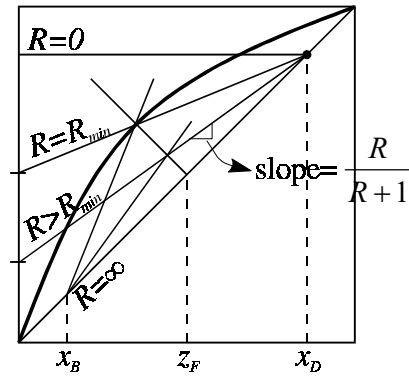
An important part of the design of any distillation column is the choice of reflux ratio. There are a few qualitative considerations which must be kept in mind.

1) Existence of R_{min}

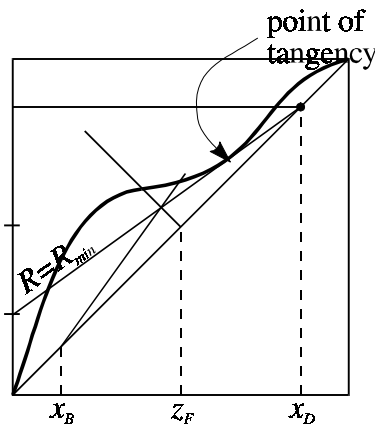
The first thing you should know is that there is a minimum value that the reflux can assume and still achieve the desired separation. Recall that the slope of the ROL is

$$\text{slope of ROL} = \frac{R}{R+1}$$

Notice that, as R is reduced, the intersection of the ROL and the Q-line moves toward the equilibrium curve. As it does so, the



minimum number of stages required approaches infinity for the reasons mentioned above: you can never get to the intersection of the operating line and the equilibrium curve.



Usually this **minimum reflux ratio** can be determined using the point of intersection between the q-line and the equilibrium curve. On some peculiar xy diagrams the R.O.L. or S.O.L. constructed in this way might cross the equilibrium curve at points other than where the Q-line crosses. Then the reflux ratio must be increased until neither operating line crosses equilibrium curve before reaching the q-line. Of course, the operating line can be tangent to the equilibrium curve.

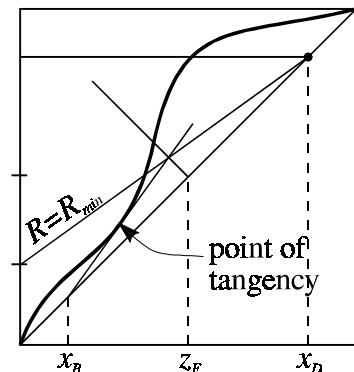
This point of tangency is called a **pinch point**. In stepping off the stages, it will take an infinite number just to reach the pinch, but if the reflux ratio is increased every so slightly, then the separation can be achieved, although the number of stages might be large.

minimum reflux ratio -- smallest value of R for which the desired separation can be achieved with a finite number of stages.

The pinch point might also occur on the S.O.L. as shown at right. Regardless of where the pinch occurs, once you have drawn the q-line and operating lines, the minimum reflux ratio (thus determined graphically) can be calculated from (11.4-24) in Geankoplis:

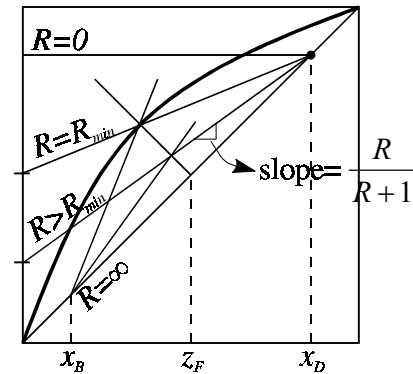
$$R_{min} = \frac{x_D - y'}{y' - x'} \tag{76}$$

where (x',y') is any point on the R.O.L. (x',y') can be chosen for convenience: for example, you might want to choose the y-intercept.



To determine the minimum reflux ratio using the McCabe-Thiele method, we might imagine drawing the ROL and SOL on the xy -diagram starting with a high reflux ratio (where ROL and SOL coincide with 45° line) and then decrease the reflux ratio until any one of three things happens:

1. the ROL becomes tangent to the equilibrium curve
2. the SOL becomes tangent to the equilibrium curve
3. the intersection of the ROL and SOL occurs on the equilibrium curve



An important thing to notice about the minimum reflux ratio is that, as we approach it, the number of stages approaches infinity:

$$\text{as } R \rightarrow R_{\min}, N \rightarrow \infty$$

Clearly you don't want to operate near the minimum reflux ratio because it would cost too much to build a column with so many stages. Generally as you increase the reflux ratio, both operating lines move away from the equilibrium curve so that the steps become larger. Then fewer stages will be needed.

$$\text{as } R \uparrow, N \downarrow$$

2) Total Reflux: $R \rightarrow \infty$ gives Minimum Stages

In the limit that R approaches infinity, the y -intercept of the R.O.L. becomes zero. The R.O.L. becomes the 45° line. Of course, the S.O.L. and R.O.L. always intersect along the q -line, which means that the S.O.L. also becomes the 45° line. This is the furthest the operating lines can ever be from the equilibrium curve, so this condition gives the minimum number of stages:

$$\text{as } R \rightarrow \infty: \quad \text{R.O.L.} \rightarrow \text{S.O.L.} \rightarrow 45^\circ\text{-line}$$

$$\text{and} \quad N \rightarrow N_{\min}$$

Although it might appear that this is the best value of the reflux ratio, it turns out that there is a "dark side" to this solution. The problem is what is happening to flowrates inside the column.

$$\text{Recall} \quad R \equiv L/D$$

Now to get infinite reflux ratio, one of two things has to happen:

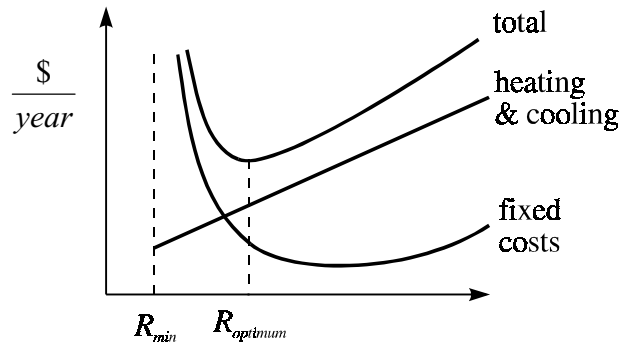
$$R \rightarrow \infty: \quad L \rightarrow \infty \text{ or } D \rightarrow 0$$

In most designs, you are interested in processing a fixed amount of material, this implies that F, D , and B are fixed, which eliminates the second alternative above. A simple mass balance about the split of L and D tells us that the vapor flowrate must also get very large:

$$L \rightarrow \infty: \quad V \rightarrow \infty, q_c \rightarrow \infty, q_r \rightarrow \infty, \text{tower diameter} \rightarrow \infty$$

This means that the heat exchanger for both the condenser and the reboiler are getting very large as are the cost of utilities (steam and cooling water).

Thus the costs of building the tower becomes large either near the minimum reflux ratio (where the height of the tower becomes large) or near total reflux (where the diameter of the column becomes large). The costs of utilities increase about linearly with reflux ratio.



The total costs will experience a minimum at some reflux ratio, which we call the

optimum reflux ratio: minimizes total costs/year

Typically the optimum occurs for:

$$1.1 < R_{opt}/R_{min} < 1.5$$

However most plants actually operate at slightly larger R since the additional cost is not very much and it buys you flexibility in case you decide later you want to change x_D or in case the feed composition changes, you have some room to maneuver:

$$1.2 < R/R_{min} < 2.0$$

CALCULATING FLOWRATES AND CONDENSER/REBOILER HEAT DUTIES

To compute the heat duties of the condenser and reboiler, we will need to know the flowrates in various parts of the column. We will start at the top of the column and work our way down. First we use the definition of reflux ratio:

$$L = RD \quad \text{and} \quad V = (R+1)D \quad (77)$$

Given F or D and the composition of the three streams (x_D , z_F and x_B), we can determine the two unknown flowrates just by doing a total mole balance and a component mole balance over the entire distillation column (the blue system in and figure at right).

$$\begin{aligned} F &= D + B \\ z_F F &= x_D D + x_B B \end{aligned}$$

Solving these two equations for the two unknown flowrates, we obtain

$$F = \frac{x_D - x_B}{z_F - x_B} D$$

and

$$B = \frac{x_D - x_F}{x_D - x_B} F = \frac{x_D - x_F}{z_F - x_B} D \quad (79)$$

Given F , x_D , z_F and x_B , we can thus calculate D , V and L . In a total condenser, we are condensing all of the overhead vapor. Assuming the condenser output is a saturated liquid, the condenser heat duty is just

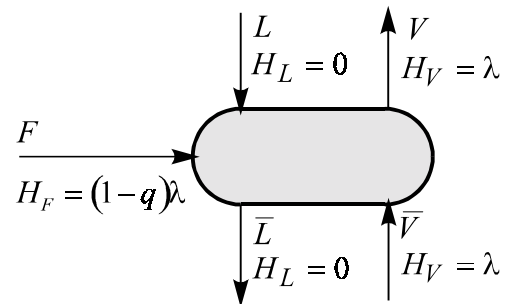
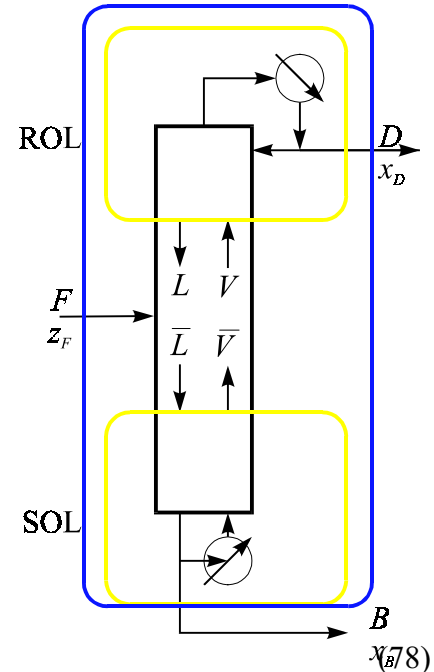
$$q_c = V\lambda$$

To calculate the reboiler heat duty, we need to evaluate \bar{V} . A look at the streams entering the feed plate (see figure at right), we realize that we have at least two unknowns \bar{L} and \bar{V} . A total mole balance gives:

$$\bar{V} + F + L = V + \bar{L}$$

which represents only one relationship in two unknowns. The remaining relationship is obtained from an enthalpy balance about the feed tray:

$$FH_F + LH_L + \bar{V}H_V = \bar{L}H_L + VH_V$$



Our analysis of countercurrent cascades is based on the equimolar overflow assumption, which contains some assumptions about enthalpy: see "Constant Molar Overflow" on p71. In particular, we neglect sensible heat and assume that all components have the same latent heat of vaporization, then we can evaluate the enthalpies of all saturated liquid or saturated vapor streams as:

$$H_L = 0, H_V = \lambda$$

Recall the definition of q from p81. This allows us to express the enthalpy of the feed in terms of q :

$$q \equiv \frac{H_V - H_F}{H_V - H_L} = \frac{\lambda - H_F}{\lambda} \quad \text{or} \quad H_F = (1-q)\lambda$$

Substituting the values for enthalpy into the enthalpy balance about the feed plate gives:

$$F(1-q)\lambda + \bar{V}\lambda = V\lambda \quad \text{or} \quad \boxed{\frac{V - \bar{V}}{F} = 1 - q} \quad (80)$$

Substituting this into the total mole balance and dividing by F :

$$\frac{\bar{L} - L}{F} = 1 + \underbrace{\frac{\bar{V} - V}{F}}_{q-1} \quad \text{or} \quad \boxed{\frac{\bar{L} - L}{F} = q} \quad (81)$$

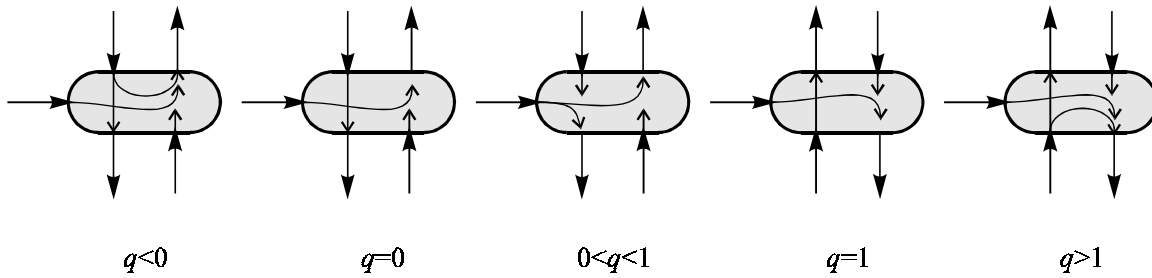
Thus introducing the feed onto a plate causes a discontinuity in the flowrates of liquid and vapor in the column. Although the flowrates are the same for each stage in the cascade above the feed, and the same for each stage in the cascade below the feed, the flowrates are different in the two cascades. For example, for a saturated liquid feed, $q=1$, and the liquid leaving the feed tray has a higher flowrate than entering by an amount equal to the feed flow rate:

$$\text{for } q=1: \quad \bar{L} - L = qF = F \quad \text{and} \quad V - \bar{V} = (1-q)F = 0$$

whereas the vapor flow is unchanged. On the hand, if the feed is saturated vapor, then the vapor flowrate leaving the stage will be higher than entering by an amount equal to the feed rate.

$$\text{for } q=0: \quad \bar{L} - L = 0 \quad \text{and} \quad V - \bar{V} = F$$

The flows for other thermal conditions of the feed are summarized graphically below:



Knowing all the flowrates, we can now calculate the reboiler heat duty. The reboiler has to boil all the vapor sent into the bottom cascade. For a partial reboiler (where the bottoms product is withdrawn from the liquid remaining in the kettle), there can be no superheating of the vapor (it must be a saturated vapor). Then the reboiler heat duty is

$$q_r = \bar{V}\lambda$$

ROLE OF Q-LINE

Recall (see “Step 4” on p81) that we said one point of the SOL is the intersection of the q -line (QL) and the ROL. In this section, we present the arguments supporting this claim.

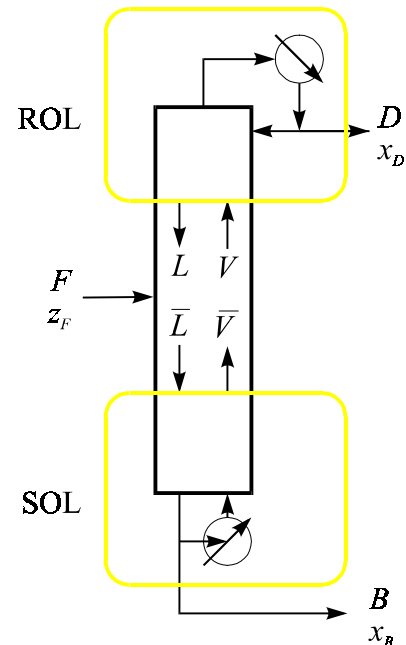
The equations of the operating lines are obtained by performing a mole balance on component A between some pair of streams in the middle of the column and the end of the column away from the feed (balances use the systems denoted by the yellow lines):

$$\text{R.O.L.:} \quad Vy = Lx + Dx_D \quad (82)$$

$$\text{S.O.L.:} \quad \bar{V}y = \bar{L}x - Bx_B \quad (83)$$

We claim that the q -line represents the intersection of these two lines. Think of these as two equations in two unknowns (x,y) . The point of intersection of these two lines is that point (x,y) which simultaneously satisfies both equations.

Now we are not going to try to solve these two equations for (x,y) . But we can find other linear relationships between x and y by combining these two equations. One linear combination is particularly convenient in that it yields an equation which we can plot without knowing any of the flowrates that appear in (82) and (83):



$$(83) \text{ minus } (82): \quad (\bar{V} - V)y = (\bar{L} - L)x - (Bx_B + Dx_D)$$

Notice that the last term in this equation represents the total rate of component A leaving the tower. This must equal the total rate at which A enters the tower. So the above becomes:

$$(\bar{V} - V)y = (\bar{L} - L)x - Fz_F$$

Dividing by F gives:

$$\underbrace{\frac{\bar{V} - V}{F}}_{q-1} y = \underbrace{\frac{\bar{L} - L}{F}}_q x - z_F$$

$$\text{Substituting (80) and (81):} \quad (q-1)y = qx - z_F$$

$$\text{or} \quad y = \left(\frac{q}{q-1} \right) x + \frac{z_F}{1-q}$$

which is the equation of our q -line. This equation represents a linear combination of the two equations which are satisfied at the intersection of the two operating lines. Thus this equation must also be satisfied at that point. It turns out that that QL represents the locus of intersections of the ROL and SOL for different reflux ratios.

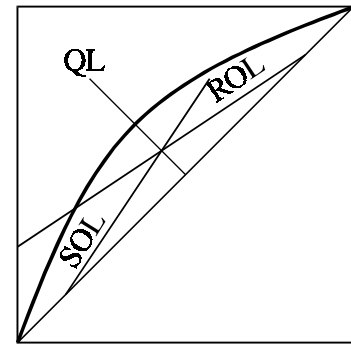
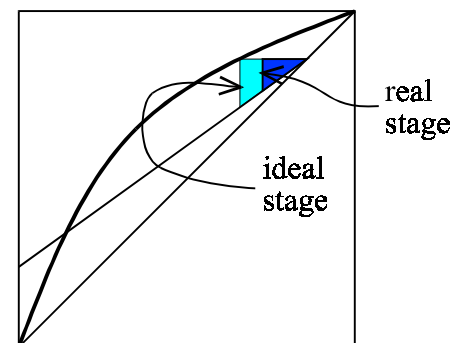


PLATE EFFICIENCY

So far we have always assumed that the vapor and liquid streams leaving a given stage are at equilibrium. In stepping off the stages, we have always gone all the way from the operating line to the equilibrium curve. If the contacting of the two phases on the tray is good (that is, if the area of contact is large and the time of contact is long) we can approach this ideal state, but we will never quite reach it. For a nonequilibrium stage, our horizontal step will be a little shorter than for an ideal stage. Of course, we still end up at a point on the operating line, because this represents a mole balance which must still be satisfied.



Because the real steps are shorter, it will take more of them to achieve the same separation. The ratio of the number of ideal to real stages required will be less than one and is called the:

$$\text{overall (column) efficiency} \text{ -- } N_{ideal}/N_{real} \equiv E_{oc} < 1$$

While this efficiency is easy to use, the value of the efficiency is hard to determine. A more fundamental quantity is the

Murphree (tray) efficiency --

$$\frac{y_n - y_{n+1}}{y_n^* - y_{n+1}} \equiv E_{My} \quad (84)$$

where

y_n = actual y leaving stage n

y_n^* = y in equil with x_n

On an xy diagram, this represents the height of a real step divided by the height of an ideal step for the same x_n . Alternatively, one could also define efficiency based on the change in liquid composition (rather than vapor composition):

$$E_{Mx} \equiv \frac{x_{n-1} - x_n}{x_{n-1} - x_n^*} \quad (85)$$

This definition is based on the width of a step (involves changes in x) rather than based on the height of a step (changes in y) as in (84).

Some typical values of plate efficiencies are given in Table 18-4 (taken from Perry's 6th edition).

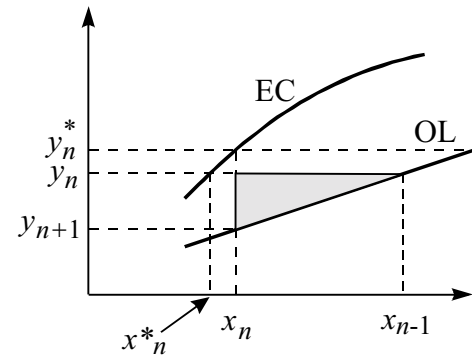
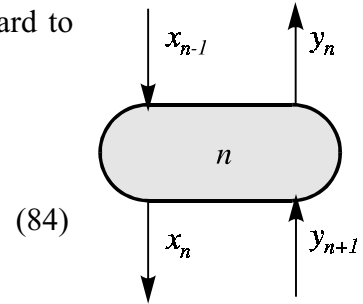


Table 18-4 Representative Plate Efficiencies

Disperser	System	Column diameter, ft	Tray spacing, in	Pressure, psia	Static submergence, in	Efficiency, %		Remarks	Ref.	
						E_{mo} *	E_{oc} †			
Bubble cap	Ethanol-water	1.31	10.6	14.7	1.18	83-87	1	
		1.31	16.3	14.7	1.18	84-97			
	Methanol-water	2.5	14	14.7	1.2	80-85	2	
		3.2	15.7	14.7	1.0	90-95	3	
		2.6	19.7	1.9	0.2	55-68	4	
		Cyclohexane-n-heptane	4.0	24	14.7	0.25	65-90	5
					24	50	4.25	65-90
	Cyclohexane-n-heptane	4.0	24	5	0.6	65-85	Tunnel caps	6	
				24		75-100			
				24	14.7	1.5	70-80		
Ripple sieve	Benzene-toluene	1.5	15.7	14.7	1.5	70-80	7	
		5.0	24	14.7	0.4	60-80	8	
Ripple sieve	Methanol-water	3.2	15.7	14.7	70-90	10.8% open	3	
		2.5	14	14.7	1.0	75-85	10.4%	2	
	Methanol-water	3.2	15.7	14.7	1.57	90-100	4.8% open	3	
		2.6	19.7	1.9	0.75	70	12.3% open	9	
	Benzene-toluene	1.5	15.7	14.7	3.0	60-80	18% open	7	
	Methyl alcohol-n-propyl alcohol-sec-butyl alcohol	6.0	18	18	1.38	64	10	
	Mixed xylenes + C ₈ -C ₁₀ paraffins and naphthenes	13.0	21	25	1.25	86	5	
		4.0	24	5	2.0	60-70	14% open	13	
	Isobutane-n-butane	4.0	24	5	2.0	70-80	14% open	13	
		4.0	24	165	2.0	110	8% open	12	
		4.0	24	165	2.0	120	14% open	13	
4.0		24	300	2.0	110	8% open	12		
4.0		24	400	2.0	100	8% open	12		
Turbogrid valve	Methanol-water	3.2	15.7	14.7	70-80	14.7% open	3	
		2.5	14	14.7	1.0	75-85	2	
	Ethyl benzene-styrene	2.6	19.7	1.9	0.75	75-85	4	
		4.0	24	20	3.0	50-96	Rect. valves	11	
	n-Butane-isobutene	4.0	24	165	3.0	104-121	Rect. valves	11	
		1.5	15.7	14.7	3.0	75-80	7	

References

- Kirschbaum, *Z. Ver. Dtsch. Ing. Beih. Verfahrenstech.*, (5), 131 (1938); (3), 69 (1940).
- Kirschbaum, *Distillier-Rektifizierteknik*, 4th ed., Springer-Verlag, Berlin and Heidelberg, 1969.
- Kastanek and Standart, *Sep. Sci.*, 2, 439 (1967).
- Billet and Raichle, *Chem. Ing. Tech.*, 38, 825 (1966); 40, 377 (1968).
- AIChE Research Committee, *Tray Efficiency in Distillation Columns*, final report, University of Delaware, Newark, 1958.
- Raichle and Billet, *Chem. Ing. Tech.*, 35, 831 (1963).
- Zuiderweg, Verborg, and Gilissen, *Proc. Intn. Symp.*, Brighton, England, 1960.
- Manning, Marple, and Hinds, *Ind. Eng. Chem.*, 49, 2051 (1957).
- Billet, *Proc. Intn. Symp.*, Brighton, England, 1970.
- Mayfield, Church, Green, Lee, and Rasmussen, *Ind. Eng. Chem.*, 44, 2238 (1952).
- Fractionation Research, Inc., "Report of Tests of Nutter Type B Float Valve Tray," July 2, 1964, from Nutter Engineering Co., Tulsa.
- Sakata and Yanagi, *Inst. Chem. Eng. Symp. Ser.*, no. 56, 3.2/21 (1979).
- Yanagi and Sakata, *Ind. Eng. Chem. Process Des. Dev.* 21, 712 (1982).

*See Eq. (18-32).

†See Eq. (18-28).

NOTE: To convert feet to meters, multiply by 0.3048; to convert inches to centimeters, multiply by 2.54; and to convert pounds-force per square inch to kilopascals, multiply by 6.895.

DETERMINING NUMBER OF REAL STAGES

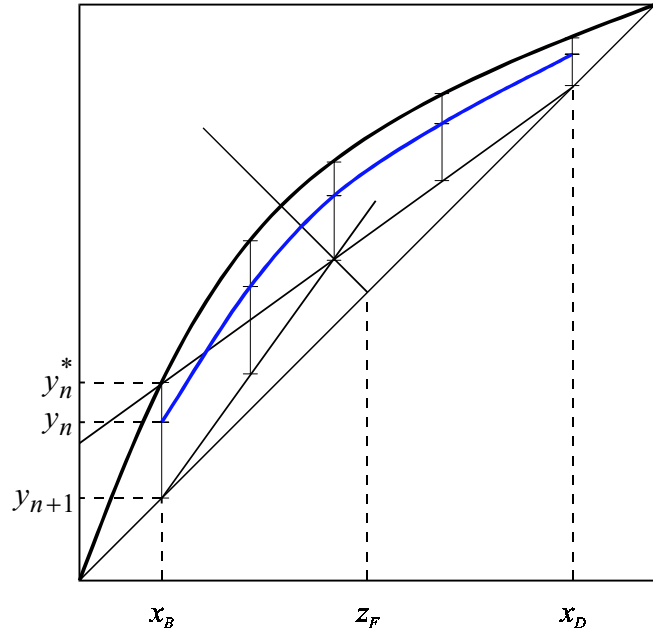
Suppose we have a value for E_{Mx} or E_{My} , how do we use it to determine the number of real stages required? The procedure is similar to that for ideal stages:

Steps 1-6) same as for ideal stages

We locate the two operating lines and the q-line, just as before. But before we step off the stages we use the efficiency to determine a new curve between the operating lines and the equilibrium curve.

Step 7) Plot psuedo-equilibrium curve using either (84) or (85).

The blue curve in the xy-diagram at right was drawn using (84). At several x-values between x_B and x_D , we draw a vertical line between the lowest operating line and the equilibrium curve. On each of these line segments, we locate a point which is a fraction of the distance up the line segment from the bottom, where that fraction equals the plate efficiencies. The locus of these points is the **psuedo-equilibrium curve**.



Finally, we step off the stages as before, but using the psuedo-equilibrium curve in place of the true equilibrium curve.

Step 8) Step off stages between operating lines and pseudo-equilibrium curve.

Since we used definition (84) based on the vapor mole fractions, we should start our stepping process at the bottom of the column, rather than the top. In other words, we start at (x_B, x_B) and step upwards until either the vapor or the liquid mole fraction exceeds x_D . By stepping from the bottom up, the step from the operating line toward the equilibrium curve involves changes in y , whereas when we step from the top down, the step from the operating line toward the equilibrium curve involves changes in x instead of y . The latter is appropriate when the efficiency is defined in terms of x instead of y .

Chapter 12. Multi-Component Distillation

The objective of distillation is the separation of the feed into streams of nearly pure products. In binary distillation, we have two components and two product streams. With more than two components in the feed, there is no way to achieve this with a single column (a single column might have a third product stream, but its composition would never be nearly pure).

To separate a mixture of three components into three nearly pure streams, we will need at least two separate distillation columns to get three streams. In general, if there are N_c components, we will need $N_c - 1$ columns.

N_c components

$N_c - 1$ columns

This assumes that each column can achieve a sharp separation between two components of adjacent volatility.

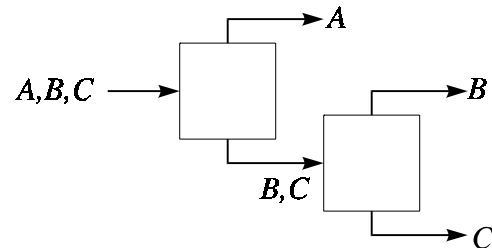
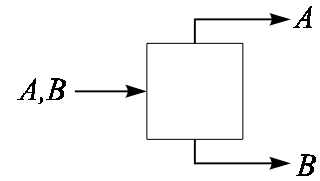
Alternatively, the designer might try to first split off component C in the first column — rather than A . The choice between these two alternatives is a matter of experience. One “rule of thumb” is to perform the easiest separations first. In this course, we will focus instead on the design of the individual columns after this decision has been made.

The first step in the design of a single column is to specify the product distribution. Let A, B, C, \dots denote components ranked in order of decreasing volatility.

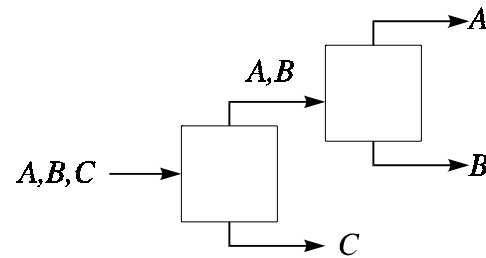
sharp split -- distillate contains only components A-M, while bottoms contains only components N-Z

In any real distillation, all components will be found in all product streams in at least trace amounts. When we say “only” components A-M are found in the distillate, we usually mean that the mole fractions of the remaining components (i.e. N-Z) can be neglected when summing the mole fractions to unity.

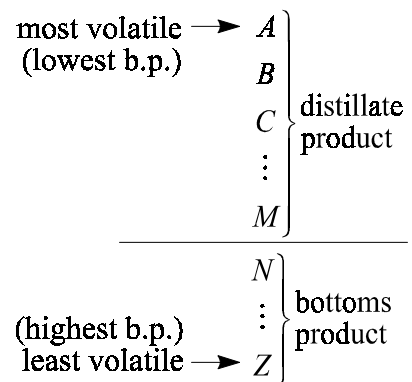
Sharp separations are not always possible, but we will focus on



Alternative #1



Alternative #2



them in this introduction, for the sake of simplicity. In the description above, components M and N play a special role and are called

key components -- M,N (for sharp split)

The more volatile of the two is called the light key, while the other is the heavy key:

light key -- M

heavy key -- N

PRODUCT DISTRIBUTION FOR A SHARP SPLIT

EXAMPLE #1: A mixture with 33% hexane, 37% heptane and 30% octane is to be distilled to give a distillate product of 1% heptane and a bottoms product of 1% hexane. Find D/F , B/F , and x_{Di} , x_{Bi} for the other components.

Solution: First we arrange the list of components in order of relative volatility. In this case, that is easy since we have a homologous series* of alkanes. Since vapor pressure general drops with molecular weight in any homologous series, we don't need to consult tables of boiling points or vapor pressures to order the components.

Component	Formula	
hexane	C_6H_{14}	most volatile
heptane	C_7H_{16}	
octane	C_8H_{18}	least volatile

Let's take a basis of 100 moles of feed ($F=100$) and try to fill out the following table:

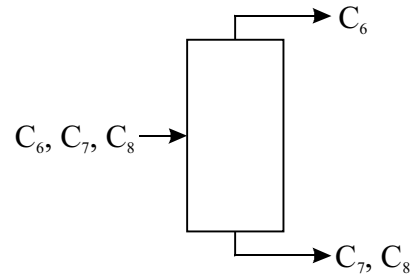
Component	Fz_{Fj}	z_{Fj}	Dx_{Di}	x_{Di}	Bx_{Bi}	x_{Bi}	
hexane	33	0.33	--	--	--	0.01	light key
heptane	37	0.37	--	0.01	--	--	heavy key
octane	30	0.30	--	--	--	--	
totals =	100	1	D	1	B	1	

Comment: Generally the more volatile components end up in the distillate stream and the less volatile components in the bottoms. Being the most volatile, most of the hexane is expected to end up in the distillate; we are told that the bottoms actually contains a little hexane ($x_{B6} = 0.01$). Heptane is of intermediate volatility and so might end up in either or both streams. From the

* A "homologous series" is a set of very similar items, which differ in some property. In this case, the series is a set of components of similar molecular structure (the alkanes) which differ only in the number of CH_2 groups in the chain.

problem statement, we also know that the distillate contains a little heptane ($x_{B7} = 0.01$) and so presumably most of the heptane ends up in the bottoms. Being less volatile than heptane, we can reasonably assume that all of the octane ends up in the bottoms.

In essence, we are then making a sharp split between hexane and heptane with the “1%” values specifying the sharpness of the split desired. In other words, hexane has been chosen as the light key and heptane as the heavy key. If we assume that there is virtually no octane in the distillate (octane is heavier than the heavy key), then we can finish specifying the composition of the distillate stream.



Component	Fz_{Fi}	z_{Fi}	Dx_{Di}	x_{Di}	Bx_{Bi}	x_{Bi}
hexane	33	0.33	--	0.99	--	0.01
heptane	37	0.37	--	0.01	--	--
octane	30	0.30	0	0	30	--
totals =	100	1	D	1	B	1

Knowing the concentration of hexane in both of the product streams allows us to determine the flowrates from mole balances:

$$\text{component } C_6: \quad 0.99D + 0.01B = 33$$

$$\text{total:} \quad D + B = 100$$

$$\text{Solving simultaneously:} \quad D = 32.65, B = 67.35$$

Component	Fz_{Fi}	z_{Fi}	Dx_{Di}	x_{Di}	Bx_{Bi}	x_{Bi}
hexane	33	0.33	32.32	0.99	0.67	0.01
heptane	37	0.37		0.01		--
octane	30	0.30	0	0	30	--
totals =	100	1	32.65	1	67.35	1

Now using the fact that the balance of the distillate and bottoms streams must be heptane, we can fill out the table:

Component	Fz_{Fi}	z_{Fi}	Dx_{Di}	x_{Di}	Bx_{Bi}	x_{Bi}
hexane	33	0.33	32.32	0.99	0.67	0.01
heptane	37	0.37	0.33	0.01	36.67	0.5445
octane	30	0.30	0	0	30	0.4454
totals =	100	1	32.65	1	67.35	1

Comment #1: In this example we have completed the specifications of the two product streams for a 3-component mixture in which the *sharpness of split* was specified by giving the mole fraction of the heavy key in the distillate stream and the mole fraction of the light key in the bottoms. Alternatively, we might have been given the recovery* of the two key components in either product stream.

Comment #2: The only additional information that is needed if the number of components is larger than 3 is the mole fraction of those components in the feed. The initial guess for the distribution of additional components in the product streams is determined by the following rules:

Rule 1) Components heavier than the heavy key
are assumed to end up in entirely in the bottoms

Rule 2) Components lighter than the light key are assumed to end up in entirely in the distillate

MINIMUM NUMBER OF TRAYS

Now let's see if we can get some idea of how many trays we will need. This is a difficult problem to do precisely. What can be done relatively easily is to estimate the number of trays needed at *total reflux* -- this is the minimum number of trays. Some gross assumptions:

total reflux: $D \approx 0$, $L \approx V$

equal molal overflow: $L = V = \text{const}$ for all trays

constant relative volatilities: $\alpha_{ij} = \text{const}$ for all trays

Recall
$$\alpha_{ij} \equiv \frac{K_i}{K_j} \quad (86)$$

is the *relative volatility* of component i compared to j , where

*For example, "5% of the heavy key is recovered in the distillate" means $Dx_{D,HK} = 0.05 \times Fz_{F,HK}$.

$$K_i \equiv \frac{y_i}{x_i} \quad (87)$$

is the **distribution coefficient** for component i (or j). With these assumptions, we can start at the top of the column and work out the compositions of streams leaving every stage.

For a total condenser:

$$y_{1i} = x_{0i} = x_{Di} \quad (88)$$

for $i=1, \dots, N_c$. The first subscript is the stage number (as in binary mixtures) and the second subscript is the component. With all the compositions of the vapor stream leaving stage 1 known, we can determine the compositions of the exit liquid stream from the known values of the relative volatility:

$$\alpha_{ij} \equiv \frac{K_i}{K_j} = \frac{y_{1i}/x_{1i}}{y_{1j}/x_{1j}}$$

or

$$\frac{x_{1i}}{x_{1j}} = \frac{1}{\alpha_{ij}} \frac{y_{1i}}{y_{1j}} = \alpha_{ji} \frac{y_{1i}}{y_{1j}} \quad (89)$$

Substituting (88):

$$\frac{x_{1i}}{x_{1j}} = \alpha_{ji} \frac{x_{Di}}{x_{Dj}} \quad (90)$$

for each component i . Notice that if $i=j$, (1) yields

for $i=j$:

$$\frac{x_{1i}}{1} = \underbrace{\alpha_{ii}}_1 \frac{x_{Di}}{1} \quad \text{or} \quad 1 = 1$$

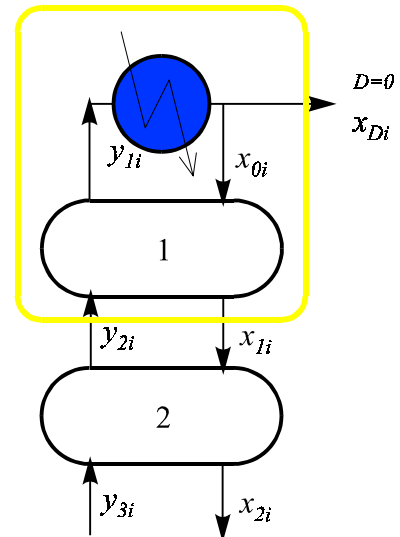
which doesn't tell us anything new; thus we have only N_c-1 independent relations of this type instead of N_c . Choosing one element as the reference (say $j=N_c$), we can write N_c-1 relations for the N_c-1 independent mole fractions. The missing equation is $\sum x_{1i} = 1$. Thus the composition of the liquid leaving tray 1 has been completely determined.

Next we determine y_{2i} by mole balances.

component i :

$$Vy_{2i} = Dx_{Di} + Lx_{1i}$$

but for total reflux $D \approx 0$ so that $L \approx V$, leaving:



$$y_{2i} = x_{1i} \quad (91)$$

for $i=1, \dots, N_c$. Knowing the composition of the vapor leaving stage 2, we can calculate the composition of the liquid from the known volatilities.

Rewriting (89), replacing the stage number 1 by 2:

$$\frac{x_{2i}}{x_{2j}} = \alpha_{ji} \frac{y_{2i}}{y_{2j}}$$

from (91):

$$\frac{x_{2i}}{x_{2j}} = \alpha_{ji} \frac{x_{1i}}{x_{1j}}$$

Using (90):

$$\frac{x_{2i}}{x_{2j}} = \alpha_{ji}^2 \frac{x_{Di}}{x_{Dj}} \quad (92)$$

From (90) and (92), we begin to see a trend. The generalization of this trend yields:

$$\frac{x_{ni}}{x_{nj}} = \alpha_{ji}^n \frac{x_{Di}}{x_{Dj}}$$

In particular, we are interested in the number of steps required to get from the distillate to the bottoms:

$$\frac{x_{Bi}}{x_{Bj}} = \alpha_{ji}^{N_{\min}} \frac{x_{Di}}{x_{Dj}}$$

The exponent represents the minimum number of steps on the xy diagram. One of these steps is the partial reboiler. Solving for N_{\min} :

$$N_{\min} = \frac{\ln\left(\frac{x_{Di}/x_{Bi}}{x_{Dj}/x_{Bj}}\right)}{\ln(\alpha_{ij})}$$

which is called *Fenske's equation*. Now in any real system, the relative volatility will not be constant. One way to patch things up is to use some kind of average volatility:

$$\alpha_{ij} = \sqrt{\alpha_{Dij} \alpha_{Bij}}$$

where α_{Dij} and α_{Bij} are evaluated at the bubble-points of the distillate or bottoms, respectively. In this case, an appropriate mean is the geometric mean of the volatilities evaluated at the conditions of the distillate and bottoms compositions. We use the bubble-point temperature

rather than the dew-point temperature because the distillate and bottoms streams are usually saturated liquids. If they were saturated vapors, then we would use the dew-point instead.

Example #2. Calculate the N_{min} for the separation in Example #1 if the column is operated at 1.2 atm.

Solution:

Evaluating the relative volatilities

We start by evaluating the relative volatilities in the feed, distillate and bottoms streams knowing their composition and thermal state.

Time out: Vapor pressure data for pure components is available in the CRC handbook. C6, C7 and C8 form a nearly ideal mixture and Raoult's law applies:

$$p_i = x_i P_i^o$$

where p_i is the partial pressure and P_i^o is the vapor pressure. Then the distribution coefficient can be calculated from

$$K_i = \frac{y_i}{x_i} = \frac{p_i/P}{x_i} = \frac{x_i P_i^o}{x_i P} = \frac{P_i^o}{P} \quad (93)$$

and the relative volatility from

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{P_i^o/P}{P_j^o/P} = \frac{P_i^o}{P_j^o} \quad (94)$$

Vapor pressure depends very strongly on temperature: recall the **Clausius-Clapeyron equation** (S&VN, p182):

$$\frac{d \ln P_i^o}{dT} = \frac{\lambda_i}{RT^2} \quad \text{or} \quad \frac{d \ln P_i^o}{d(1/T)} = \frac{\lambda_i}{R}$$

where λ_i is the molar heat of vaporization of the pure component. Integrating this with respect to T (ignoring the weak temperature dependence of λ_i) yields

$$\ln P_i^o = A_i - \frac{\lambda_i}{RT} \quad (95)$$

or

$$P_i^o(T) = A_i' \exp\left(-\frac{\lambda_i}{RT}\right) \quad (96)$$

where A_i is just some integration constant. Note the exponential sensitivity of vapor pressure to temperature. Vapor pressure data is often summarized in handbooks (e.g. *Lange's Handbook of Chemistry*, 13th edition, pages 10-29 to 10-54) using **Antoine's equation**:

$$\ln P_i^0 = A_i - \frac{B_i}{T + C_i} \quad (97)$$

which is a semi-empirical generalization of (95) that accounts for the variation of λ_i with T . Other handbooks (e.g. *CRC Handbook of Chemistry & Physics*, 57th edition, pages D-183 to D-215) give vapor pressures at several temperatures and leave you to develop your own interpolation scheme.

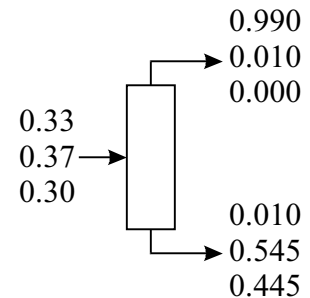
Since vapor pressure depends strongly on temperature, so does the partition coefficient K_i given by (93). However, the relative volatility α is much less dependent on temperature. The reason becomes clear when we substitute (96) into (94):

$$\alpha_{ij} \equiv \frac{P_i^o}{P_j^o} = \frac{A_i'}{A_j'} \exp\left(-\frac{\lambda_i - \lambda_j}{RT}\right)$$

Note that when the two molar heats of vaporization are equal, the temperature-dependence vanishes. Even if they are only approximately equal, the temperature-dependence of the relative volatility will be much less than of the vapor pressures. For this reason, the assumption of **constant relative volatility** is frequently used.

Time in: We took the values of the vapor pressure of each component given in CRC handbook and fit them to (97) to find the constants A_i , B_i and C_i for each component.

Now the distillate is a saturated liquid containing nearly pure hexane, so its temperature is near the boiling point of hexane at 1.2 atm (the pressure throughout the column) or 75°C.



Component	x_D	P_i^o (atm)	$K_i = P_i^o / P$	$\alpha_{i,HK} = K_i / K_{HK}$
C6	0.990	1.200	1.000	2.574
C7	0.010	0.466	0.388	1.000
C8	0.000	0.187	0.156	0.401

The bubble point of the bottoms is 115°C (see Geankoplis p681-2 for how to determine bubble points for multicomponent mixtures):

Component	x_B	P_i^o (atm)	$K_i = P_i^o/P$	$\alpha_{i,HK} = K_i/K_{HK}$
C6	0.010	3.448	2.873	2.236
C7	0.544	1.542	1.285	1.000
C8	0.446	0.723	0.603	0.469

Calculate Minimum Stages

To calculate N_{min} , Fenske's equation is usually applied to the heavy key and the light keys. So we are interested in $\alpha_{LK,HK}$

$$\alpha_{67} = \sqrt{2.574 \times 2.236} = 2.399$$

Fenske's equation is

$$N_{min} = \frac{\ln\left(\frac{x_{Di}/x_{Bi}}{x_{Dj}/x_{Bj}}\right)}{\ln(\alpha_{ij})} = \frac{\ln\left(\frac{0.99/0.01}{0.01/0.544}\right)}{\ln(2.399)} = 9.82$$

So at an absolute minimum, we need 10 ideal steps, or 9 ideal stages plus the reboiler. Knowing the number of trays, we can also use Fenske's equation to check if indeed the octane fraction in the distillate is negligible as we assumed in Example #1.

$$\alpha_{87} = \sqrt{0.401 \times 0.469} = 0.434$$

$$N_{min} = 10 = \frac{\ln\left(\frac{x_{D8}/0.446}{0.01/0.544}\right)}{\ln(0.434)}$$

Solving for x_{D8} , we obtain

$$x_{D8} = 1.93 \times 10^{-6}$$

which indeed is negligible compared to the other mole fractions in the distillate.

MINIMUM REFLUX RATIO

Method 1) Pseudo-Binary Method

Assuming a saturated liquid feed ($q=1$) and constant relative volatility, the minimum reflux ratio turns out to be

$$R_{\min} = \frac{\frac{x_D}{z_F} - \alpha_{AB} \frac{1-x_D}{1-z_F}}{\alpha_{AB} - 1} \quad (98)$$

where x_D and z_F are the molefraction of the light key in the psuedo-binary mixture and $1-x_D$ and $1-z_F$ are the molefraction of the heavy key in the psuedo-binary mixture:

$$z_F = \frac{z_{F,LK}}{z_{F,LK} + z_{F,HK}} \quad \text{and} \quad 1 - z_F = \frac{z_{F,HK}}{z_{F,LK} + z_{F,HK}}$$

where $z_{F,LK}$ and $z_{F,HK}$ are the mole fractions in the multi-component mixture.*

Proof: We can obtain the minimum reflux ratio from the point of intersection of the q -line and the equilibrium curve. Recall (76) from page 89:

$$R_{\min} = \frac{x_D - y'}{y' - x'} \quad (99)$$

which was derived using two points on the ROL to determine the slope and knowing that the slope is $R/(R+1)$. For a saturated liquid feed, the q -line is vertical so that

$$x' = z_F \quad (100)$$

The y -coordinate of this point is determined knowing that (x', y') lies on the equilibrium curve. For constant relative volatility, we can express the equilibrium curve as a simple equation using the definition of relative volatility:

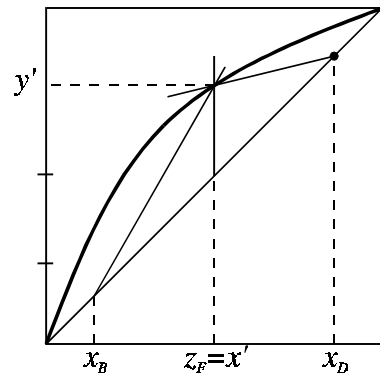
$$\alpha_{AB} \equiv \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B} = \frac{y/(1-y)}{x/(1-x)}$$

Solving for y :

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

Substituting $x = x' = z_F$, we can calculate

$$y' = \frac{\alpha_{AB} z_F}{1 + (\alpha_{AB} - 1) z_F} \quad (101)$$



* To derive the relations above, take a basis of 1 mole of feed. then $z_{F,LK}$ and $z_{F,HK}$ represent the number of moles of LK and HK in the feed.

Substituting (101) and (100) into (99) leads to (98).

Method 2) Underwood's Method

This method makes similar assumptions to the psuedo-binary method except that all components are considered, not just the two key components. In particular, the assumptions made by Underwood's method are:

- 1) equimolal overflow
- 2) constant relative volatility
- 3) a sharp split with only one "pinch"

First, we will just state the method and then we will take a quick look at its proof.

Recipe:

Step 1) Find the root (denoted ϕ) in the interval $\alpha_{HK} < \phi < \alpha_{LK}$ which satisfies the polynomial (order of polynomial = number of components)

$$\sum_i \frac{\alpha_i z_{Fi}}{\alpha_i - \phi} = 1 - q \quad (102)$$

Step 2) Once we have ϕ , we can compute the minimum reflux ratio from

$$R_{\min} + 1 = \sum_i \frac{\alpha_i x_{Di}}{\alpha_i - \phi} \quad (103)$$

where the sum is just over those components present in the distillate (i.e. we ignore components heavier than the heavy key).

Proof: A mole balance on component i about the top n stages of the rectification section yields:

$$V_{n+1}y_{n+1,i} = L_n x_{n,i} + Dx_{D,i} \quad (104)$$

Recall that the distribution coefficient is defined as:

$$K_i = y_i/x_i \quad \text{or} \quad K_{n,i} = \frac{y_{n,i}}{x_{n,i}}$$

We put the tray subscript on K because its value depends on the temperature, which varies from tray to tray. Thus (104) can be rewritten as:

$$V_{n+1}y_{n+1,i} = L_n \frac{y_{n,i}}{K_{n,i}} + Dx_{D,i}$$

For **constant molal overflow**, the flowrates will be the same for each tray in the rectifying cascade, just as with binary mixtures. Thus we can drop the subscripts on flowrate.

$$Vy_{n+1,i} = L \frac{y_{n,i}}{K_{n,i}} + Dx_{D,i} \quad (105)$$

When we approach the minimum reflux ratio, we will encounter a "pinch" somewhere in the column. At the pinch, we take an infinite number of steps without changing the mole fractions:

at a pinch: $y_{n+1,i} = y_{n,i} \quad (106)$

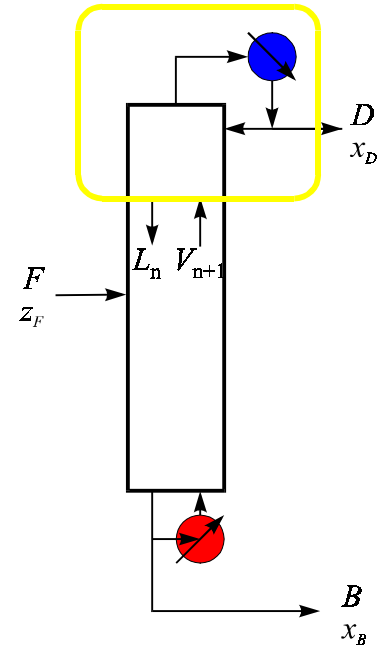
(106) into (105) and solving for y_i :

$$y_i = \frac{D}{V_\infty} \frac{x_{Di}}{1 - \frac{L_\infty}{V_\infty K_{\infty,i}}} \quad (107)$$

We have put a subscript " ∞ " on each flow rate to emphasize that this corresponds to the minimum reflux, which requires an infinite number of trays. If we require (107) to be satisfied for each component and sum over all components:

$$\sum_i y_i = 1 = \frac{D}{V_\infty} \sum_i \frac{x_{Di}}{1 - \frac{L_\infty}{V_\infty K_{\infty,i}}} \quad (108)$$

Now we can write K_i in terms of the relative volatility:



$$\alpha_i = \frac{K_i}{K_{ref}}$$

While the flowrate ratios can be related to the reflux ratio:

$$\frac{L_\infty}{V_\infty} = \frac{R_{min}}{R_{min} + 1} \quad \text{and} \quad \frac{D}{V_\infty} = \frac{1}{R_{min} + 1}$$

(108) becomes:

$$\sum_i \frac{\alpha_i x_{Di}}{\alpha_i - \phi} = R_{min} + 1 \quad (103)$$

where

$$\phi \equiv \frac{R_{min}}{K_{ref}(R_{min} + 1)}$$

If K_{ref} were known, then R_{min} could be determined as the root of this equation. Unfortunately, to calculate K_{ref} we need to know the temperature at the pinch, which is not known.

Generally there is also a pinch in the stripping section of the tower. For sharp splits, the temperature at this second pinch will be the same. We can then derive a second equation like (103) by performing our balances about the bottom n stages of the column to obtain a second equation.

$$\sum_i y_i = 1 = \frac{B}{\bar{V}_\infty} \sum_i \frac{x_{Bi}}{\frac{\bar{L}_\infty}{\bar{V}_\infty \bar{K}_{\infty,i}} - 1}$$

where the overbars denotes flowrates in the stripping section. Then we will have two equations and two unknowns: K_{ref} and R_{min} . Their solution is the value of ϕ which satisfies the following equation:

$$\sum_i \frac{\alpha_i z_{F,i}}{\alpha_i - \phi} = 1 - q$$

where $z_{F,i}$ is the composition of the feed and q is its thermal condition. There are several ϕ 's which satisfy this equation. It turns out that we want:

$$\alpha_{HK} < \phi < \alpha_{LK}$$

Once ϕ is determined, we can calculate R_{min} from (103). This is called **Underwood's method**.

Example #3. Calculate the R_{min} for the separation in Examples #1 and #2 if the feed is 60% vapor ($q = 0.4$).

Solution: Recall the feed and product compositions (see sketch at right). Using Underwood's method, we first determine the root of (102).

$$\sum_i \frac{\alpha_i z F_i}{\alpha_i - \phi} = 1 - q$$

Substituting into known values:

$$\underbrace{\frac{2.399 \times 0.33}{2.399 - \phi} + \frac{1 \times 0.37}{1 - \phi} + \frac{0.434 \times 0.30}{0.434 - \phi}}_{f(\phi)} = 1 - 0.4$$

which is a cubic equation. The left-hand side $f(\phi)$ is plotted at right. This equation has three singular points at

$$\phi = \alpha_1, \alpha_2 \text{ and } \alpha_3$$

These are shown as the 3 vertical lines in the plot. Notice that there are also 3 different ϕ 's for which

$$f(\phi) = 1 - q = 0.6$$

We are interested in the root in the interval:

$$\alpha_{HK} < \phi < \alpha_{LK} \quad \text{or} \quad 1 < \phi < 2.399$$

which turns to be $\phi = 1.739$. Once we have the value of ϕ , we calculate the reflux ratio from (103):

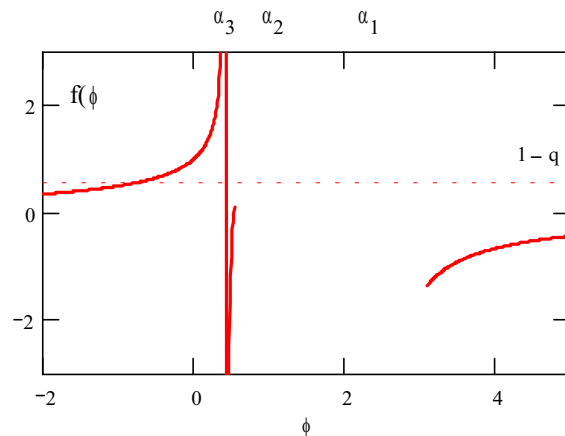
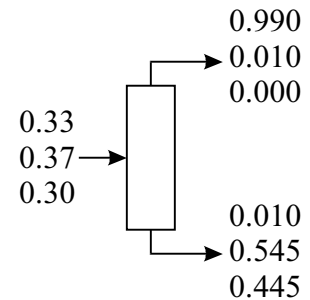
$$R_{\min} + 1 = \sum_i \frac{\alpha_i x_{Di}}{\alpha_i - \phi}$$

where the sum only includes those components present in significant quantities in the distillate. In this case, octane (which is heavier than the heavy key) was neglected in the distillate for Example #1. It should also be neglected in this sum, although in this case, it's inclusion does not change the result.

$$R_{\min} + 1 = \frac{2.399 \times 0.99}{2.399 - 1.739} + \frac{1 \times 0.09}{1 - 1.739} = 3.59$$

ANSWER:

$$R_{\min} = 2.59$$



NUMBER OF IDEAL PLATES AT OPERATING REFLUX

Ref: MSH p588-609

Method 1) Underwood's method

Underwood's method can be extended to calculate the number of plates analytically when the equal molal overflow assumption and constant relativity are appropriate. But even then, the calculations are sufficiently involved that a computer would be helpful. If we are going to use a computer, we might as well do the rigorous tray-by-tray calculations (see Method 3); thus we will not extend Underwood's method further in these Notes.

Method 2) Gilliland correlation

An empirical but much easier to use method is the **Gilliland correlation**. This is an empirical relation between the number of ideal stages and the operating reflux ratio. You also need to know the minimum number of ideal stages (at total reflux) and the minimum reflux ratio. Because of its simplicity, this correlation is widely used for preliminary estimates.

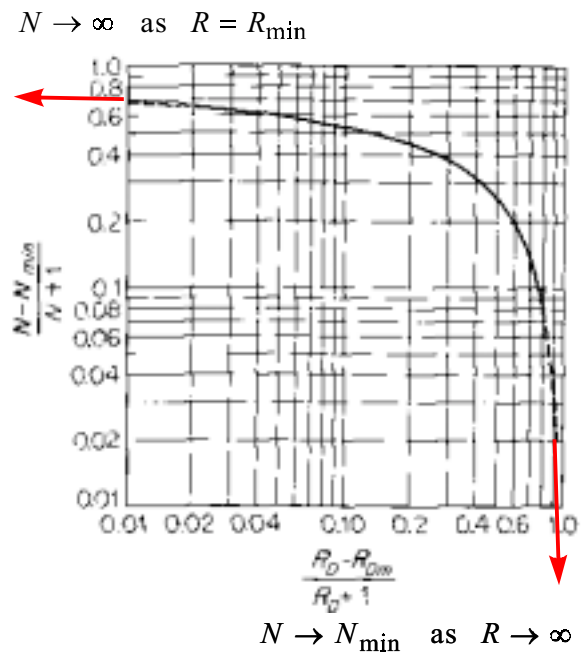
A second type of empirical correlation is Erbar & Maddox (see Fig. 11.7-3 in Geankoplis):

$$\frac{N_{\min}}{N} = f\left(\frac{R}{R+1}, \frac{R_{\min}}{R_{\min}+1}\right)$$

Method 3) Rigorous Solution of MESH Equations

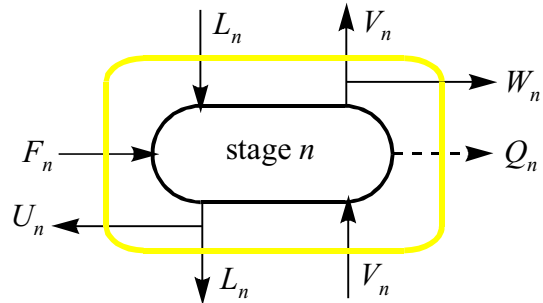
Reference: Henley & Seader, *Equilibrium-Stage Separation Operations in Chemical Engineering*, Chpt. 15.

The final design of multistage equipment to multicomponent distillation usually requires rigorous determination of temperatures, flow rates, and compositions at each stage. This must be done numerically by computer. We will use a computer program called CHEMSEP to look at a couple of typical columns. Although the program is designed to be used like a "black-box", I'd like to give you a little peek at what goes on inside.



A rigorous mathematical description of a multistage cascade involves material and energy balances and some representation of the vapor-liquid equilibrium. The resulting set of algebraic equations is called the **MESH Equations**, for reasons which will soon become apparent.

Consider a general stage in the cascade, which we will label stage n . It has the usual liquid and vapor streams entering and leaving. It might also be a feed stage, in which case $F_n \neq 0$. If it is not a feed stage, we just set $F_n = 0$. There might also be liquid or vapor product streams U_n or W_n as well as a heat removal Q_n . The MESH equations result from balances done about this arbitrary stage.



M Equations are Mole balances for each component i
(N_c equations for each stage):

$$L_{n-1}x_{i,n-1} + V_{n+1}y_{i,n+1} + F_n z_{i,n} = (L_n + U_n)x_{i,n} + (V_n + W_n)y_{i,n}$$

Note that the first subscript is the component i and the second subscript for the stage n .

E Equations describe the liquid-vapor Equilibrium relations among the two outlet streams, which are assumed to be at equilibrium (N_c equations for each stage):

$$y_{i,n} = K_{i,n}x_{i,n}$$

where $K_{i,n}$ is the distribution coefficients.

S Equations are the mole fraction Summations (2 equations for each stage):

$$\sum_i x_{i,n} = 1 \quad \text{and} \quad \sum_i y_{i,n} = 1$$

H Equations is the energy balance for each stage (1 equation for each stage):

$$L_{n-1}H_{L,n-1} + V_{n+1}H_{V,n+1} + F_n H_{F,n} = (L_n + U_n)H_{L,n} + (V_n + W_n)H_{V,n} + Q_n$$

If there are a total of N_s stages in the column and N_c components, then the number of equations is

$$\text{number of equations} = N_s(2N_c + 3)$$

Now we consider the following to be unknowns:

$$x_{i,n}, y_{i,n}, L_n, V_n, T_n \text{ for } i = 1, \dots, N_c \text{ and } n = 1, \dots, N_s$$

where T_n is the temperature of the liquid and vapor streams leaving stage n .

$$\text{number of unknowns} = N_s(2N_c + 3)$$

Of course, there are more variables involved in the equations. We assume that the feeds and any side drawoff flows are specified:

given:

$$F_n, z_{i,n}, H_{F,n}, U_n, W_n, Q_n$$

Also, we assume that the thermodynamic relations exists so that we can compute the enthalpy of saturated liquid and saturated vapor, given the composition, pressure and temperature:

known functions:

$$H_{L,n} = H_{L,n}(T_n, P_n, x_{1,n} \cdots x_{N_c,n})$$

$$H_{V,n} = H_{V,n}(T_n, P_n, y_{1,n} \cdots y_{N_c,n})$$

$$K_{i,n} = K(T_n, P_n; x_{1,n} \cdots x_{N_c,n})$$

Chapter 13. Computer Simulation of Distillation

We will be using a computer program called “ChemSep” to simulate distillation. Today I'd like to introduce this program. Compared with industrial software, it is user-friendly and written for student use. Below is the welcoming screen.



Arno Haket and Harry Kooijman are from the University of Technology in Delft (The Netherlands), while Ross Taylor is a Professor of Chemical Engineering at Clarkson University (New York state).

After a copyright screen, we reach the main menu:

```

File           Input           Results           Options           Help
                e   ep

F Help F      st elp F   o   F       e F   nits F  Options F  In o F       in enu

```

SOME PRELIMINARY STEPS

Although a mouse can be used with the program, the default is to use the cursor keys to move around the screen. When the desired menu item is highlighted, press ENTER to select it. You can also select menu items by typing the first letter of the desired item. Below is the result of choosing the `File` menu.

```

File           Input           Results           Options           uit
                e   ep

o
e
 e
i e to
ie
it
op
Ren e
 se
O s ell

it

F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

```

Notice that a sub-menu has appeared. You can probably guess what most of these commands do.

Before going any further, you should make sure that any files we create will be placed on the Floppy Disk drive A:\. This can be accomplished by changing the default directory to A:\. Select the `Directory` command. You will then be presented with the current directory name which can be edited to read:

```

File          Input          Results          Options          Help
ChemSep v3.50

+-----+
| Load    |
| New     |
| Save    |
| Directory|
+-----+
| Enter new directory A:\* |
+-----+
| Rename  |
| Erase   |
| DOS shell|
+-----+
| Exit    |
+-----+

F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

```

You should also save your configuration file on your floppy disk. This can be accomplished by going to the `Options` menu and selecting the `Save options` command. You should edit the file name to read "A:\ChemSep.cnf":

```

File          Input          Results          Options          Help
ChemSep v3.50

+-----+
| Solve options |
| Units         |
| Macros       |
| Interface    |
| Directories  |
| Video device |
| Output device|
| Save options  |
+-----+
| Options filename A:\ChemSep.cnf_____ |
+-----+

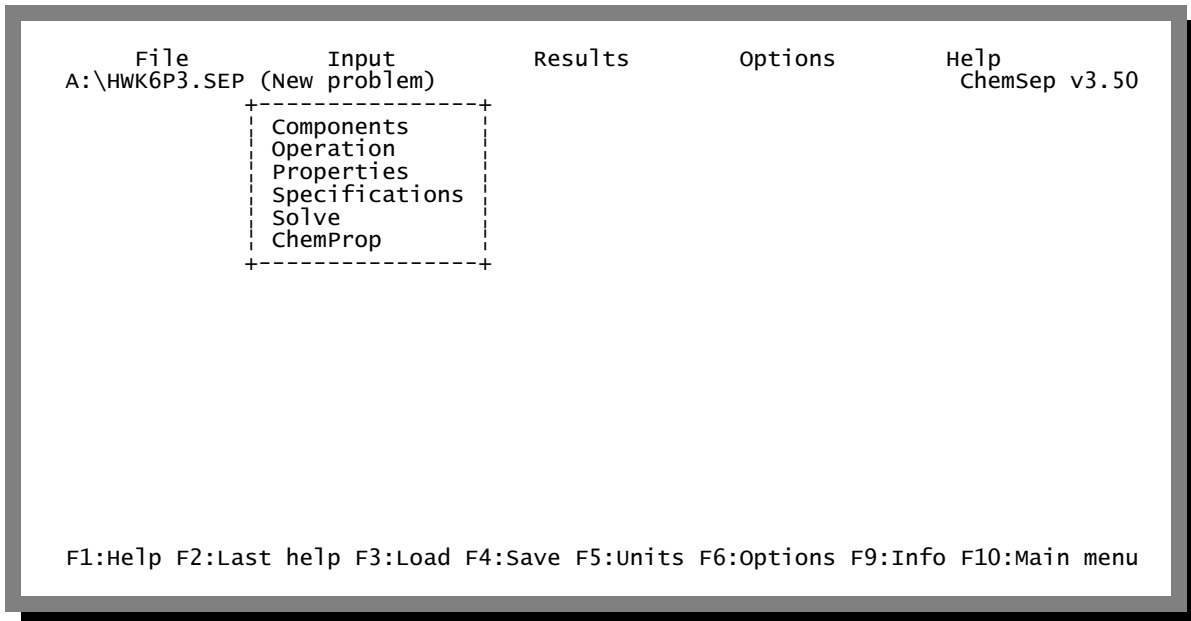
F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

```

Now any changes you make in the configuration can be saved in this file and re-loaded when you return to ChemSep at some later time.

LOADING A FILE (PROBLEM)

We are going to create a new file which simulates the solution to Prob. 3 on Hwk. #6. We start by selecting the `New` command from the `File` menu. You will then be prompted for a file name: type `"A:\HWK6P3.SEP"`. The `"A:\"` will force this file to be stored in the root directory of the floppy drive, which is the recommended location for your personal files.



The first step in inputting the problem description is to select the components. This particular homework problem is based on MS&H5 Prob. 18-3 in which we are to separate a mixture of acetone and methanol. Under the `Input` menu, select `Components`, followed by several `"Enter's"` until you are prompted for a name (see below):

```

File          Input          Results          Options          Help
A:\HWK6P3.SEP (New problem)
+-----+-----+-----+-----+
+           | Components |           | None |
+           |           |           |     |
+           | Select   |           |     |
+           | +-----+ |           |     |
+           | | Search by |           |     |
+           | | Name     |           |     |
+-----+-----+-----+-----+
+ (Substring of) name =
+-----+-----+-----+-----+
+           | Class   |           |     |
+           | Family |           |     |
+           | Property|           |     |
+-----+-----+-----+-----+

F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

```

Enter the first component name (acetone) and hit “enter”. This will bring up another short menu containing “acetone” at the bottom: Select “acetone” and hit “enter”.

```

File          Input          Results          Options          Help
A:\HWK6P3.SEP (New problem)
+-----+-----+-----+-----+
+           | Components |           | None |
+           |           |           |     |
+           | Select   |           |     |
+           | +-----+ |           |     |
+           | | Name     |           |     |
+           | | -> Restart search |           |     |
+           | | -> Refine search  |           |     |
+           | | Acetone           |           |     |
+           | +-----+ |           |     |
+           | | Return           |           |     |
+           | |           |           |     |
+-----+-----+-----+-----+

F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

```

This will add acetone to the list of components. Next select ->Restart search and type the next component name (methanol). After selecting methanol and hitting “enter”, we have two components in our list:

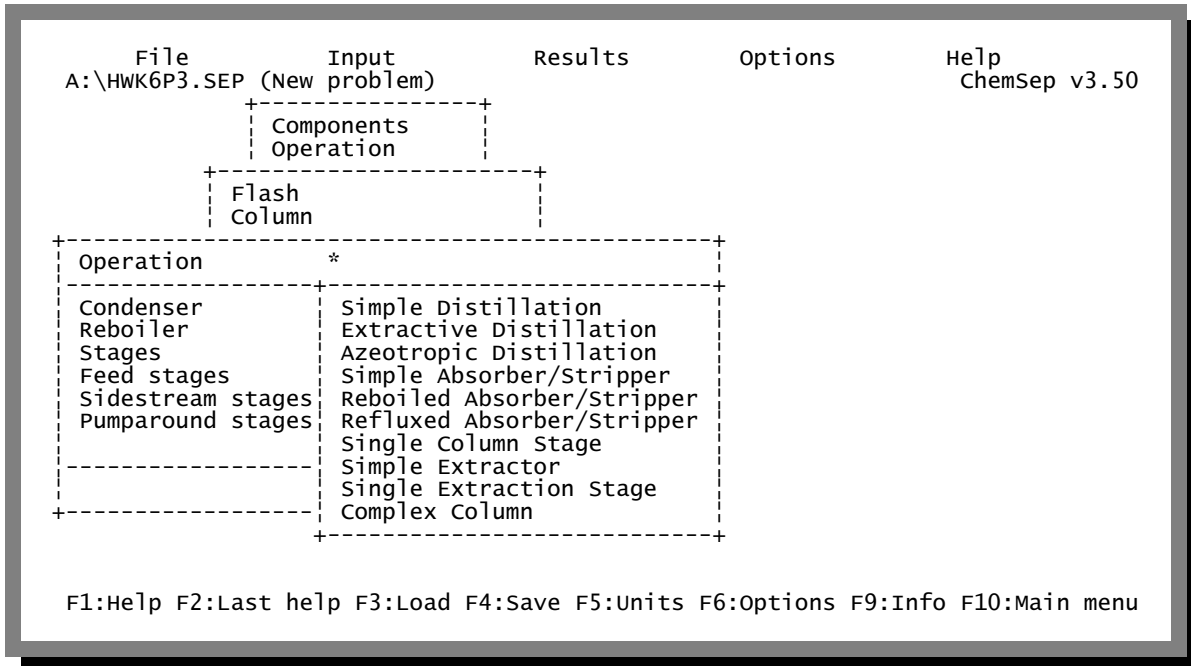

```

      File           Input           Results           Options           Help
A:\HWK6P3.SEP (New problem)
+-----+
+           | Components |           | Acetone
|           |           |           | Methanol
|           | +-----+ |           |
|           || Select  ||           +-----+
+
+-----+
| Name
|-----|
| -> Restart search
| -> Refine search
| Methanol
|-----|
| Return
|-----|

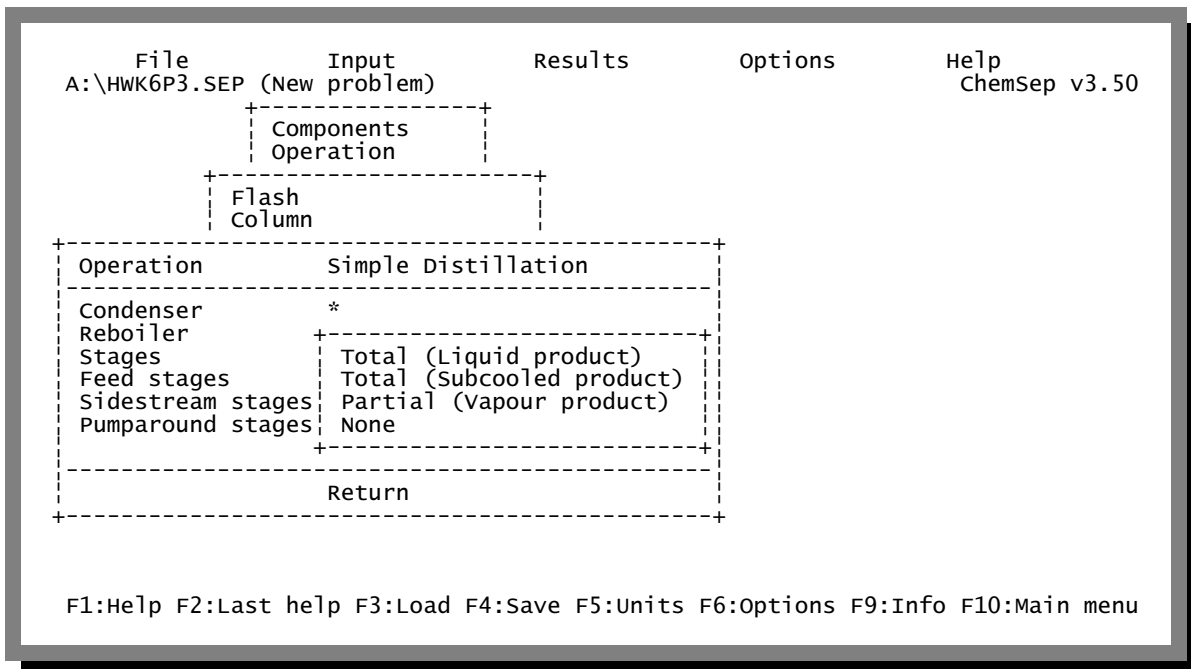
```

F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

Hit “Esc” twice brings us back to the `Input` menu. This time, select the `Operation` command, then the `Column` subcommand. The cursor is now on the “*” on the line with `Operation`. Hitting the “enter” key leads to the following screen:



Move the cursor to `simple distillation` and hit “enter”. This moves the cursor to the “*” on the line with `Condenser`. Hitting “enter” brings up a menu of options for the operation of the condenser:



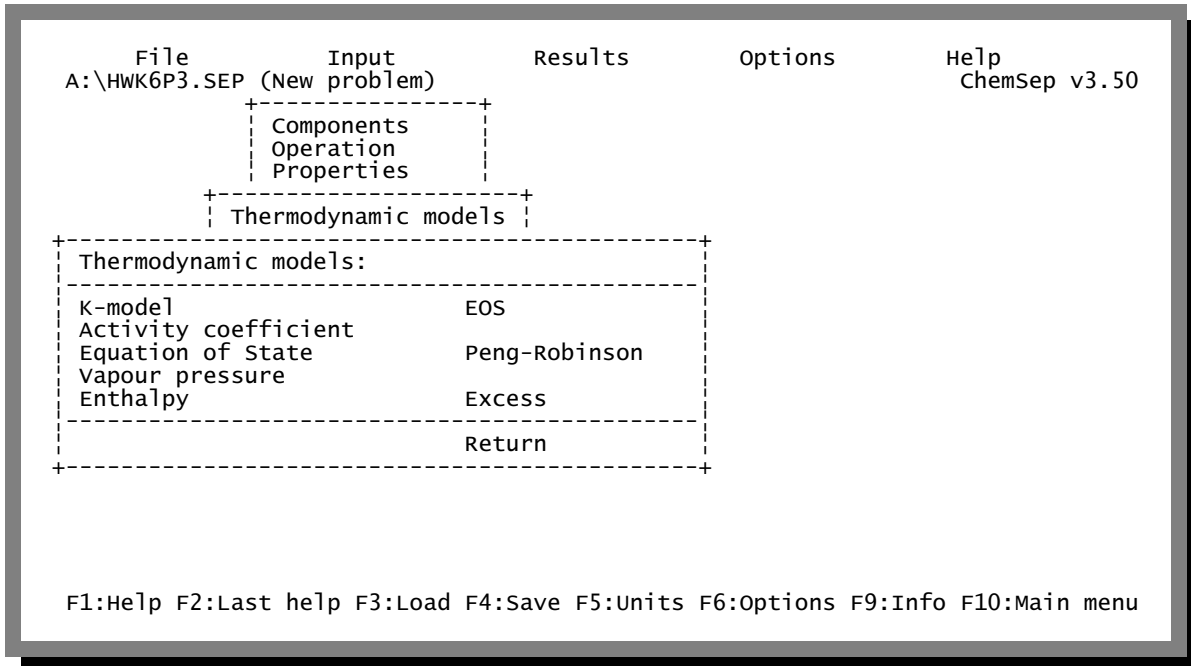
Of course, in the homework problem we want to subcool the condensate, so we choose `Total (Subcooled product)`. After making a few other choices in the remaining items, then selecting `Show flowsheet`, we have:

```

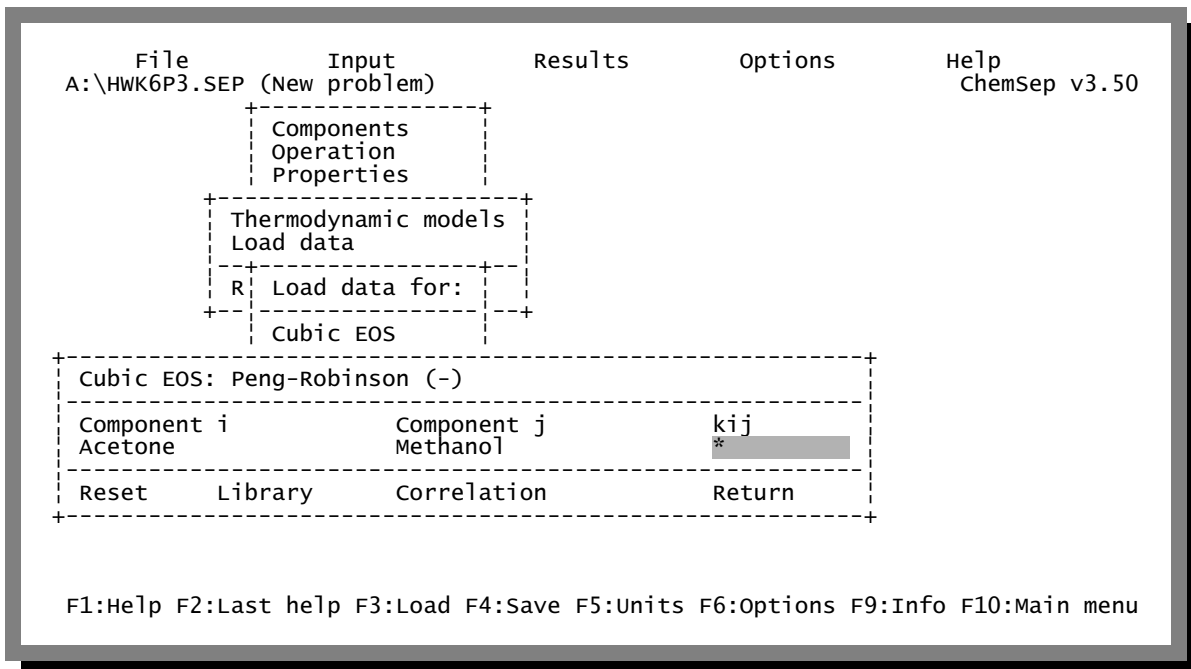
  File           Input           Results          Options          Help
A:\HWK6P3.SEP (New problem)

+-----+-----+-----+-----+
|   Components   |   |   |   |           +-----+
|   Operation    |   |   |   |           +-----+-----+ |
|-----+-----+ |   |   |   |           |           |1| |
| Flash         |   |   |   |           +-----+ +---|+
| Column       |   |   |   |           |   | +---<----->---
|-----+-----+ |   |   |   |           |---|---|---| | |
| Operation      | Simple Distillation |   |   |   |           |---|---|---|
|-----+-----+ |   |   |   |           |---|---|---|
| Condenser      | Total (Subcooled pr |   |   |   |           |---|---|---|
| Reboiler       | Partial (Liquid pro |   |   |   |           |---|---|---|
| Stages         | 23                   | ----->---17- |   |   |   |           |---|---|---|
| Feed stages    | 17                   |   |   |   |           |---|---|---|
| Sidestream stages |                   |   |   |   |           |---|---|---|
| Pumparound stages |                   |   |   |   |           | +---|-----<-----+
|               | Show flowsheet      |   |   |   |           +-----|---+ +---|+
|-----+-----+ |   |   |   |           +--->----->---
|               | Return              |   |   |   |           23+-----+
|-----+-----+ |   |   |   |           |   |   |   |
|               |                       |   |   |   |           +-----Press any key to continue-----+
|               |                       |   |   |   |           +-----+
|               |                       |   |   |   |           F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu
|               |                       |   |   |   |
+-----+-----+
  
```

We next select Return and the cursor moves to the `Properties` submenu of `Input`. Hit “enter” twice to enter the `Thermodynamic models` dialog box. Since this is not a course in thermodynamics, I will always tell you which thermo models to us. After making a few choices, the dialog box appears as follows:



Selecting `Return` takes us to the `Load data` submenu. Some thermo models do not require any further input from the user, but the cubic EOS does require a value for the interaction parameter. After selecting `Load data`, then `Cubic EOS` leads us to the following dialog:



Move the cursor to `Correlation` and hit "enter". A value for k_{ij} has been entered from the library, then select `Return`. Hitting "enter" three more times brings us back to the `Input/Specifications` submenu. Hit "enter" and choose `Pressures`. Make the selections shown as follows:

```

File      Input      Results      Options      Help
A:\HWK6P3.SEP (New problem)
          Components
          Operation
          Properties
          Specifications
          Analysis
          Pressures
-----
Pressures (atm)
Condenser pressure      1.000
Column pressure        Constant pressure
Top pressure            1.000
Pressure Drop (atm/stage)
Bottom pressure
-----
Return

F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

```

The units for pressure might not show up as atm. If not, you can change the units for entering any quantities hitting the function key F5. After setting the pressure, choose Return which moves the cursor to Heaters/Coolers. No heat is to be added or removed except for the condenser and reboiler, so we move the cursor on down to Efficiencies. Here we enter the Murphree tray efficiency. We enter "1" as the default to obtain ideal trays throughout the column.

```

File      Input      Results      Options      Help
A:\HWK6P3.SEP (New problem)
          Components
          Operation
          Properties
          Specifications
          Analysis
          Pressures
          Heaters/Coolers
          Efficiencies
-----
Murphree Efficiencies
-----
Stage Efficiency (-)
Default 1.000
-----
Insert Delete Return
-----

F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

```

Using the Insert command, we could specify different efficiencies for each tray. Choosing Return moves the cursor to the Input/Specifications/Feeds command. This is where we

specify the thermal condition, composition and flowrate of the feed. The thermal condition can be specified either as temperature and pressure or as vapor fraction and pressure. Since our feed is 70% vapor, we use the latter option. After entering the values appropriate to our problem, we have:

File	Input	Results	Options	Help
A:\HWK6P3.SEP	(New problem)			ChemSep v3.50
	Components Operation Properties Specifications			
Feed		1		
Feed stage		17		
State:		P & V		
Pressure (atm)		1.000		
Vapour fraction (-)		0.7000		
Temperature (°C)				
Flowrates (mol/s)				
Acetone		25.00		
Methanol		75.00		
Total flowrate		100.0		
Insert	Delete	Return		
F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu				

A second feed could be added using the `Insert` command. Selecting `Return`, brings us to the `Input/Specifications/Operation` command. This is where we enter specifications regarding the two remaining degrees of freedom in the column design. Hitting “enter” twice brings up a range of choices for specifying the first degree of freedom.

```

File           Input           Results           Options           Help
A:\HWK6P3.SEP (New problem)
+-----+
| Components |
| Operation  |
| Properties |
| Specifications |
+-----+
| Analysis   |
| Pressures  |
| Heaters/Coolers |
| Efficiencies |
+-----+
+--| Reflux ratio
+--| Heat duty of condenser
+
*| Distillate flow rate
D| Reflux flow rate          *
*| Component flow
--| Mole fraction of a component
| Component recovery        Return
+--| Fraction of combined feeds recovered
+
+--| Split between two components
+--| Flexible
+-----+
F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

```

We can choose only one of these. If we specify the mole fraction of acetone to be 78% (as in our problem statement), then the program adjusts the reflux ratio in an effort to obtain this composition. If we specify the reflux ratio, then the program determines the composition of the distillate product. Here we will choose the reflux ratio (to be 8.62) and see what happens. Since we specified a subcooled reflux, we next get to choose its temperature or the number of degrees of subcooling. We specify the temperature as 25°C. Hitting “enter” when the cursor is over the only remaining “*” brings up the following list:

File	Input	Results	Options	Help
A:\HWK6P3.SEP	(New problem)			ChemSep v3.50
	Components Operation Properties Specifications			
	Analysis Pressures Heaters/Coolers			
	Boilup ratio Heat duty of reboiler Temperature of reboiler			
R	Bottom product flow rate	8.620		
T	Reboiled vapour flow	25.00		
*	Component flow			
--	Mole fraction of a component			
	Component recovery	Return		
+--	Fraction of combined feeds recovered			
+	Split between two components			
	Flexible			
F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu				

Now we get to specify one property of the bottom stream. We choose to specify the mole fraction of the bottoms product. Now the `Operation` specification is complete.

File	Input	Results	Options	Help
A:\HWK6P3.SEP	(New problem)			ChemSep v3.50
	Components Operation Properties Specifications			
	Analysis Pressures Heaters/Coolers Efficiencies Feeds Operation			

	Reflux ratio (-)		8.620	
	Temperature of reflux (°C)		25.00	
	Mole fraction of a component (-)	Acetone	0.010000	

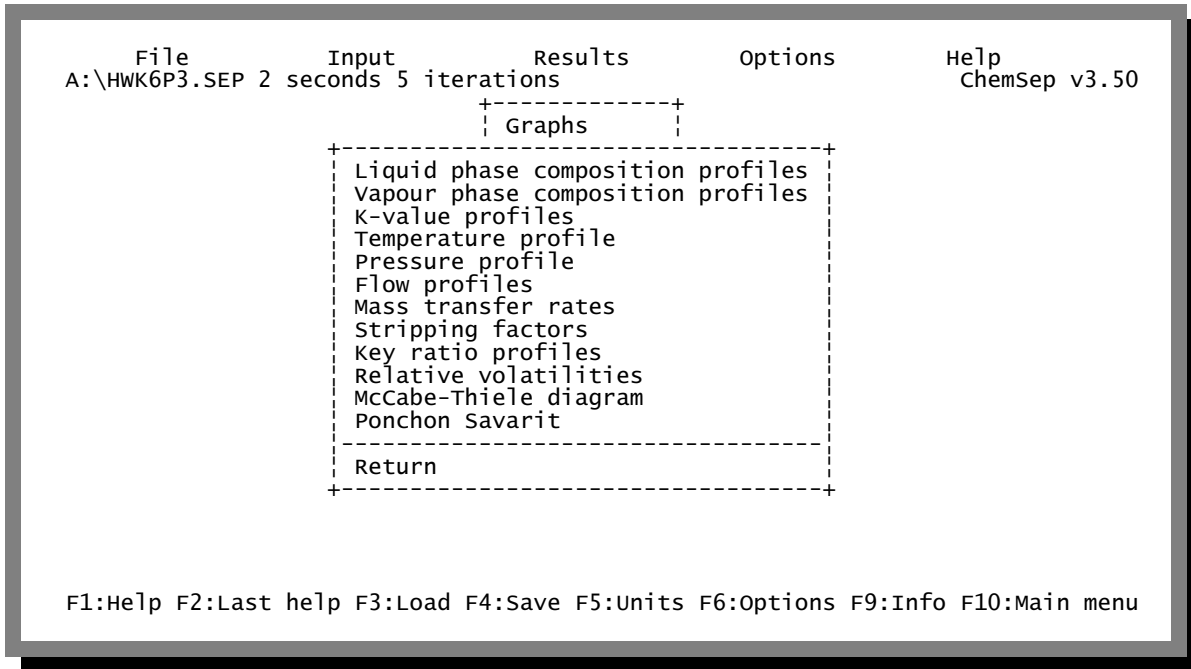
			Return	

+				
F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu				

Choosing `Return` twice places the cursor on the `Input/Solve` command. Hitting “enter”, the program saves the description and attempts to solve the MESH equations. If all the data has been entered correctly, the next screen appears:

File	Input	Results	Options	Help
A:\HWK6P3.SEP	2 seconds	5 iterations		ChemSep v3.50
		Graphs Tables Spreadsheet		
F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu				

Now we are ready to display the results. Choosing Results/Graphs gives us a menu of choices:



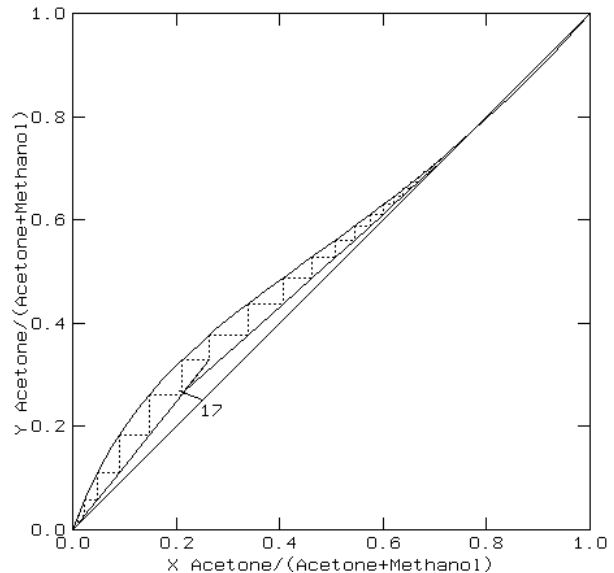
PLOTTING THE MCCABE-THIELE DIAGRAM

Let's first check out the McCabe-Thiele diagram:

The diagram at right seems to resemble that obtained in Hwkkey #6, except that the azeotrope occurs at a mole fraction of about 0.76 instead of 0.80. This difference might occur because the thermodynamic model we chose is not the best one. In any case, it means that the distillate composition will never reach the 0.78 required in Prob. 3.

Let's take a closer look at the profile. To get a better look at what's happening at the top of the column, we might want to expand that section of the McCabe-Thiele diagram. The scale as well as the format of any graph in ChemSep can be customized by hitting the SPACE key when the graph is displayed. The following dialog box appears:

McCabe-Thiele diagram for Acetone - Methanol



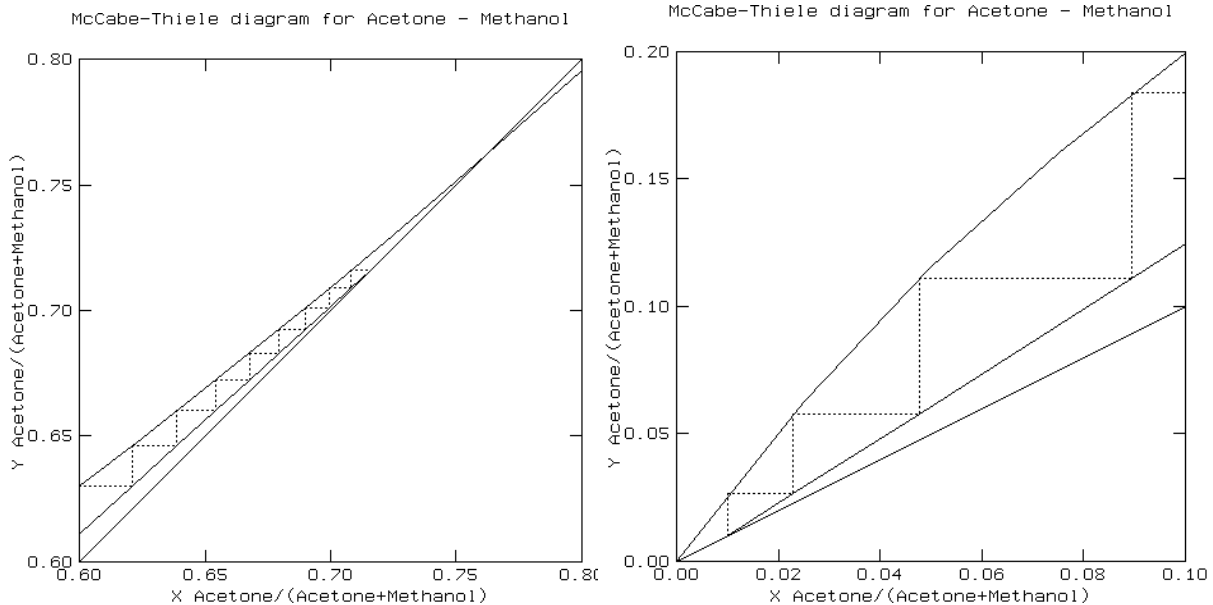
File	Input	Results	Options	Help
A:\HWK6P3.SEP	2 seconds	5 iterations		ChemSep v3.50
+-----+				

McCabe-Thiele diagram				

Title McCabe-Thiele diagram				
1st Key component Acetone				
2nd Key component Methanol				
Flip No				
Minimum/Maximum X 0 1				
X Tic interval 0.2 0				
X Label X Acetone/(Acetone+Me				
Minimum/Maximum Y 0 1				
Y Tic interval 0.2 0				
Y Label Y Acetone/(Acetone+Me				
Grid Off				
Axis color 1-Gray				
Stages lines 1-Blue :Dotted				
Equilibrium Line 1-Red :Solid				
Operating lines Yellow :Solid				
Q lines white :Solid				
Printer Setup Print				

F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu				

I have shaded the two lines which can be edited to expand the scale. Changing the range on both x and y from the interval $(0, 1)$ to the interval $(0.6, 0.8)$ and then hitting the ESC key yields the second McCabe-Thiele diagram below at the left. A second diagram appears below at right in which we have expanded the lower end of the diagram.



PRINTING THE GRAPHS

Once you get the desired graph on the screen, you probably want to make a hard copy. To print, hit the SPACE key to bring up the graph customization dialog box shown above. Notice the "Print" and "Printer Setup" items on the bottom line of the dialog. To print, you move the cursor over the "Print" item and hit the ENTER key. ChemSep will send the graph to the printer identified by the "Printer Setup" menu.

To get the graphs into this document, I instructed ChemSep to write a Windows bitmap into a file which I later imported into MS Word. I edited the "Printer Setup" (by moving the cursor over this item and hitting ENTER) to read as follows:

```

File           Input           Results           Options           Help
A:\HWK6P3.SEP 2 seconds 5 iterations
+-----+
+-----+
| McCabe-Thiele diagram
+-----+
| Title           McCabe-Thiele diagram
| 1st Key component Acetone
| 2nd Key component Methanol
| Flip           NO
| Minimum/Maximum X 0           0.1
| X Tic interval  2.0E-02  0
| X Label         X Acetone/(Acetone+Me
| Minimum/Maximum Y 0           0.2
| Y Tic interval  5.0E-02  0
| Y Label         Y Acetone/(Acetone+Me
+-----+
| Output Device Setup
+-----+
| Device         BMP
| Port           A:\TEST.BMP
| Mode           Half
| work path
+-----+
: Dotted
: Solid
: Solid
: Solid
+-----+
F1:Help F2:Last help F3:Load F4:Save F5:Units F6:Options F9:Info F10:Main menu

```

After you have Output Device Setup reading like that shown above, hit ESC to return to the graph customization dialog, select Print and hit ENTER. You will be asked to supply a filename. Use a different name for each graph.

When you "Quit" the ChemSep program, you can run Word. Bitmap files can be imported into Word using the Insert/Picture command. The picture can be cropped (eliminate unwanted portions of the picture around edges) and resized using the Format/Picture command. You can also use the mouse to do this.

- In Word6 (Office 95), "Cropping" is done with the mouse by dragging one of the six "handles" while holding down the SHIFT key. "Scaling" is done with the mouse by dragging one of the handles without using any keys. If you use one of the four corner handles for scaling, the ratio of height to width will be preserved.



- In Word7 (Office 97), "Cropping" is done with the mouse using the "Crop Tool" which is shown by the icon at right. The Crop Tool can usually be found on the Picture toolbar, which can be displayed with the View/Toolbar command.

Finally, you can position the graph anywhere on the page:

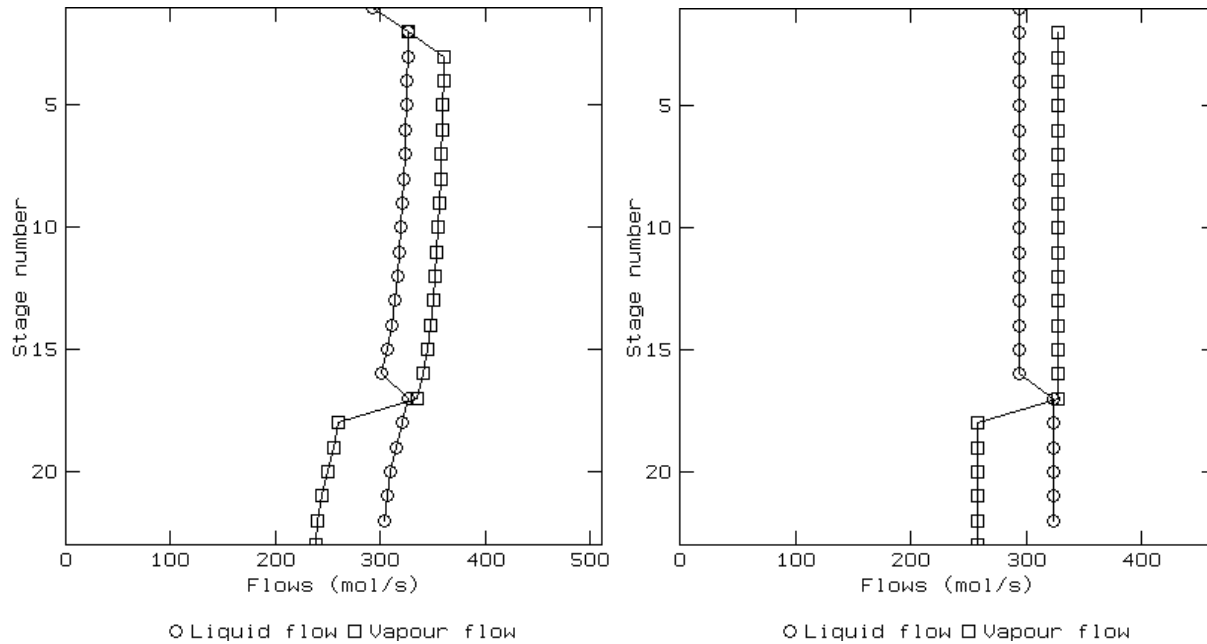
- In Word6, you can enclose the picture in a frame and then move the frame. Make sure the picture is selected (a single click of the mouse) and the six handles appear around it. Use the "Insert Frame" command from the "Insert" menu. The program might ask if you want to switch to "Page View". Answer "yes". Once in pageview, you can drag the picture to the desired position with the mouse. You can also use the "Format Frame" command to position the picture and to control "text wrapping" *etc.*
- Word7 uses Textboxes instead of frames. When inserting the picture from file, check the "Float over text" option of the Insert Picture dialog box. This puts the picture inside a Textbox which can be dragged anywhere on the page and text will wrap around it. If you have already imported the picture and did not check this box, you can still do so by selecting the picture with a single click, then use the Format/Object command. In the Format Object dialog, click on the Position tab and check the "Float over text" option.

You can add text, equations, drawings, and more bitmaps. Once you have the document looking the way you want, print it using the "File/Print" command.

TESTING THE MCCABE-THIELE METHOD

Now that we have some idea how to run ChemSep, let's use it to test the validity of the assumptions of the McCabe-Thiele method. The main assumption is "equimolal overflow." We showed that if 1) you neglect sensible heat changes compared to latent heat and 2) you assume that the latent heat of vaporization is independent of composition, then the molar flowrates of liquid and vapor streams do not vary from stage to stage.

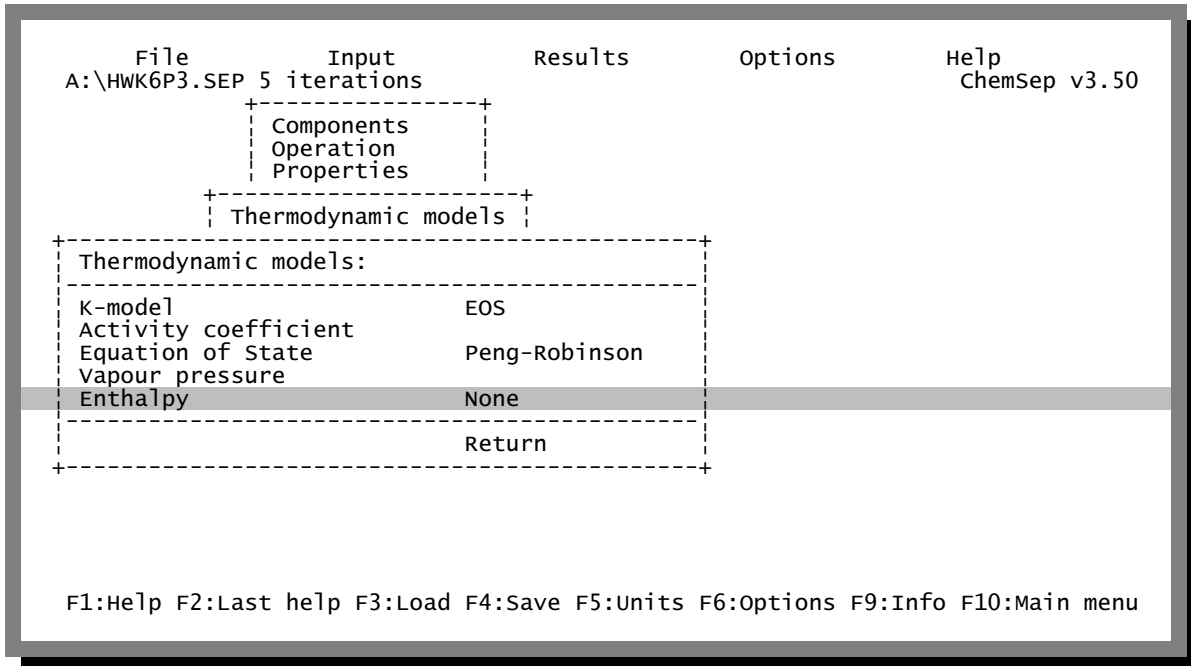
Profiles of liquid and vapor flowrates can be plotted using the `Results/Graphs/Flow Profiles` command. For the description above, we obtain the graph below on the left:



The discontinuity of flowrates on the 17th stage occurs because this is the feed tray. Because the feed is 30% liquid in the bottom cascade is higher than in the top; because the feed is 70% vapor flowrate in the top cascade is higher than in the bottom. There is also a drop in both liquid and vapor flows at the top of the column. This drop occurs because of the subcooled reflux.

Beyond the expected changes in flowrates at the feed tray and at the top, there is a continuous drop in flowrate of both streams as we move down either the rectifying cascade or the stripping cascade. These changes in flowrates within a cascade are not consistent with the *equimolar overflow* assumption.

The second graph on the right above is what would be predicted by making the equimolar overflow assumption. We forced Chemsep to make the equimolar overflow assumption by altering slightly the thermodynamic model. Navigating back to the Input/Properties/Thermo-dynamic models menu, we change the Enthalpy setting to None:



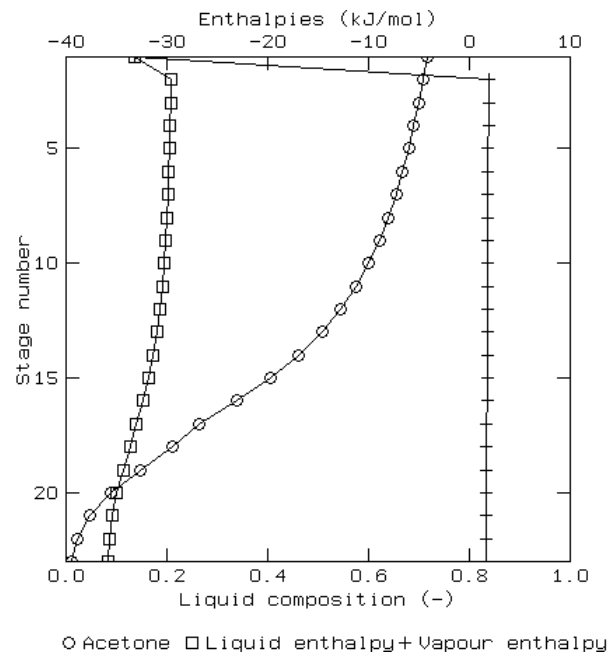
Selecting `Return` and re-solving the model leads to the flowrate profiles shown on the right side.

These variations in flowrate within a cascade stem from the fact that the enthalpy of saturated liquid is not independent of temperature or acetone content as is required for "equimolal overflow." The plot at right shows the liquid and vapor enthalpies, and the mole fraction of acetone in the liquid, versus stage number. ♣

For equimolal overflow, the enthalpy profiles should be two vertical lines. Clearly, they are not vertical lines. The departure arises because the heat of vaporization of acetone and methanol are not quite equal. The following values were read from the ChemSep library:

$$\lambda_{\text{acetone}} = 29.5 \text{ kJ/mol}$$

$$\lambda_{\text{methanol}} = 35.3 \text{ kJ/mol}$$



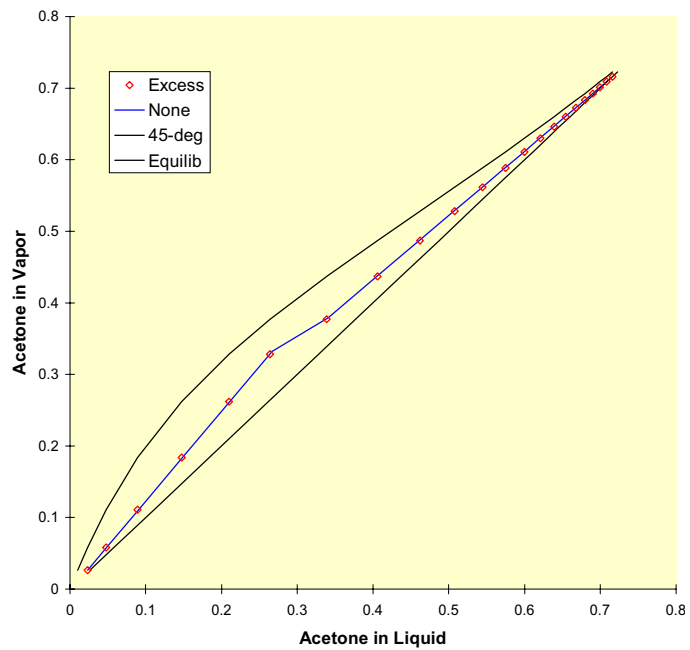
♣ To obtain these plots, I customized the "liquid phase composition profile" graph -- deleting the methanol composition, and adding the enthalpies using the "top axis" for enthalpy.

How important are these enthalpy differences? On the McCabe-Thiele diagram, these differences show up as curvature in the operating lines.

The plot at right shows points taken from the operating lines in the rigorous ChemSep separation and compares them with the ROL and SOL calculated using the McCabe-Thiele method. ♦ These calculated operating lines are the straight, solid lines on the plot.

There is very little difference. A closer examination reveals that the maximum difference in mole fraction is 0.00473, which occurs on stage 19. Put another way, the main prediction for this problem is what the distillate composition and flowrate will be

Enthalpy Model	x_D	D/F
Excess	0.7161	0.3399
None	0.7142	0.3408

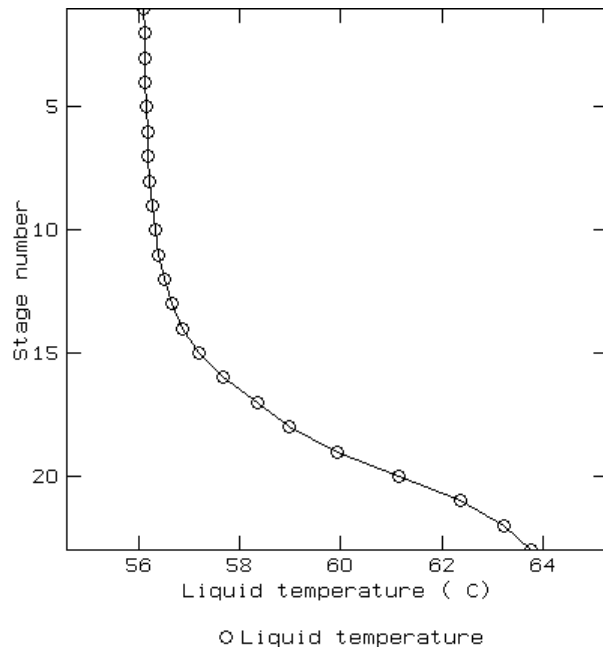


The difference between the two is insignificant. This insignificant difference is typically the case when the molar heats of vaporization differ by less than 20%.

♦ This graph was produced by EXCEL after importing the WK1 file produced by "Results Spreadsheet" menu of ChemSep.

THE TEMPERATURE PROFILE

Another interesting profile which can be plotted by ChemSep is temperature. The plot at right is obtained for the current problem. Notice that the hotter temperature occur at the bottom of the column. This is because the bottoms contain the less volatile component which has the higher boiling point.



DEGREES OF FREEDOM

ChemSep lets you specify a number of attributes of the distillate and bottoms streams. We saw this list when we specified the condenser and the reboiler. In particular, there were 10 different kinds of specifications which can be made regarding the condenser, product stream or reflux (see page 127):

1. Reflux ratio
2. Heat duty of condenser
3. Temperature of condensate
4. Distillate flow rate
5. Reflux flow rate
6. Component flow
7. Mole fraction of a component
8. Component recovery (-)
9. Fraction of combined feeds recovered (-)
10. Split between two components

There are also 10 different specifications which can also be made about the reboiler (see page 128).

1. Boilup ratio
2. Heat duty of reboiler
3. Temperature of reboiler
4. Bottom product flow rate
5. Reboiled vapour flow
6. Component flow
7. Mole fraction of a component

8. Component recovery
9. Fraction of combined feeds recovered
10. Split between two components

How many of these are independent? In ChemSep, you must specify the number of stages in each section, the pressures everywhere, and a complete description of all feeds. Then it turns out that there are really only two degrees of freedom left: there are only two additional aspects of the solution which you can specify.

We conclude by comparing the list of inputs and outputs for the two techniques we have examined. The comparison assumes we have ideal stages, constant pressure, a total condenser producing a saturated liquid product, and a partial reboiler.

Solution by McCabe-Thiele Graphical Method

Given:

1. x_D
2. desired x_B
3. $R > R_{min}$
4. N_E or use of optimum feed

Find:

1. N_S
2. (actual x_B)

Solution by Chemsep

Given:

1. x_D
2. x_B
3. N_E
4. N_S

Find:

1. R

Chapter 14. Gas Absorption/Stripping

gas absorption -- 2 components of a gas are separated by contact with a liquid (in which one component is preferentially soluble)

stripping -- 2 components of a liquid are separated by contact with a gas

An example of gas absorption is the removal of ammonia from air by contact with liquid water. Ammonia is very soluble in water whereas air is only slightly soluble.

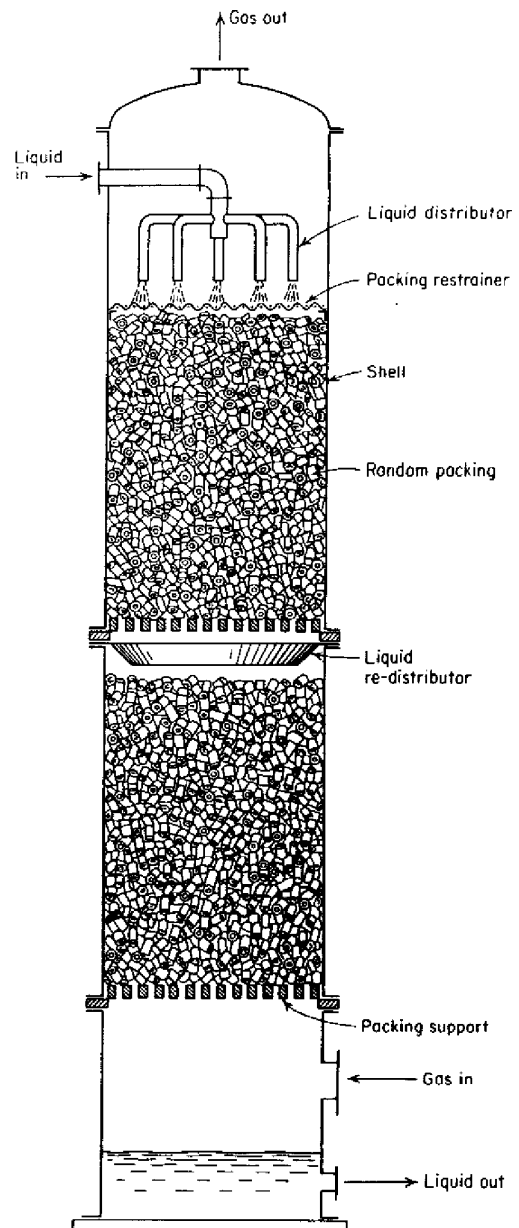
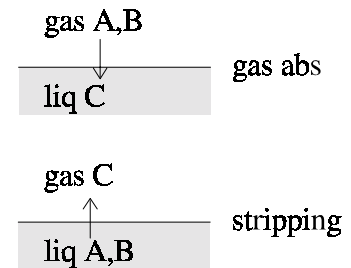
Both gas absorption and stripping involve at least three components. Usually only one of these components crosses the phase boundary. In the example of ammonia and air, ammonia is the component whose molar flowrate changes by the largest percentage of the inlet value. Although some air will also dissolve in water, and some water will evaporate into the air, the molar flowrates of air and water change by negligible fractions: their flows can usually be considered constant.

These are the two main differences between them and distillation: 1) at least 3 components, and 2) often only "one transferrable component". By contrast, in distillation, all of the components are present in both phases.

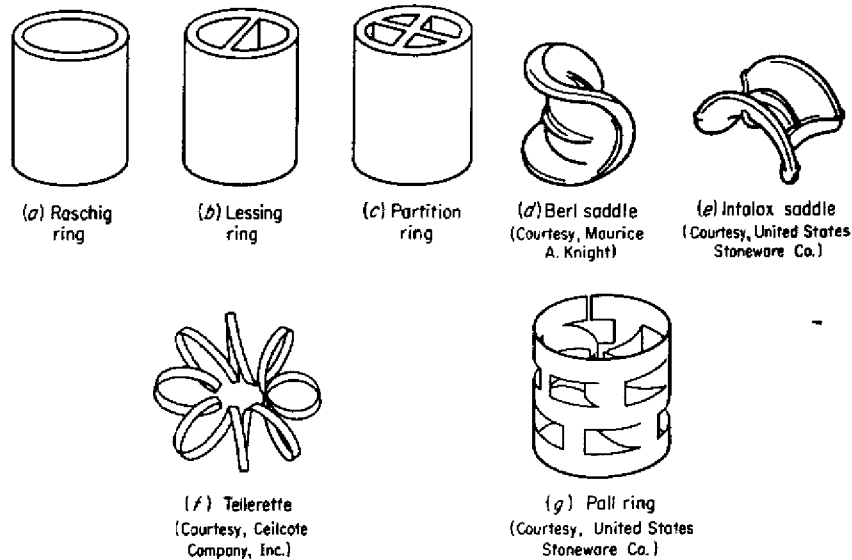
EQUIPMENT FOR ABSORPTION/STRIPPING

Although liquid and gas streams for absorption or stripping could be contacted using a tray column (like that used in distillation), tray columns are seldom used. The reason is that tray efficiencies are generally much lower for absorption and stripping than for distillation (perhaps only 5% instead of 50%).

Because of this very low efficiency, very large numbers of trays are required -- perhaps 100's or 1000's. Fabrication costs just become prohibitively expensive. Fortunately, a viable alternative exists: the packed tower.



A *packed tower* is simply a tube or pipe, which is filled with some sort of "packing." The packing typically consists of particles around an inch in diameter. In commercial packed towers, the usual choice are particles with one of three different shapes:



- raschig ring (which is just a piece of pipe which has been cut into segments, whose length and diameter are about the same)

$$L \approx D \approx \frac{1}{2} \text{ to } 1\frac{1}{2} \text{ inches}$$

- Berl saddle
- Pall ring

Although, in a pinch, almost anything you have laying around would do -- ping-pong balls, golf balls, etc. The purpose of the packing is to promote good contact between the liquid and vapor streams which are being brought together to permit interfacial mass transfer.

The liquid stream is usually fed into the top of the tower while the vapor is fed into the bottom. Thus we have countercurrent flow of the two streams, which has the same advantages for mass transfer as it did for heat transfer.

The packing promotes good contact between the phases by dividing the two feed streams into many parallel interconnected paths. Ideally, you would like the liquid to flow downward as a thin film over the surface of the packing. This would give the maximum surface area of contact between the gas and liquid.

If you just pour the liquid from the end of the pipe onto the top of the packing in tower having much larger diameter than the pipe, most of the packing will not even be wet. Only some of the channels will be carrying flow. This is called:

channeling -- maldistribution of liquid flow

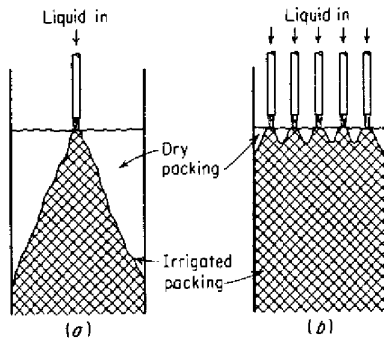


Fig. 6.23 Liquid distribution and packing irrigation (a) Inadequate; (b) adequate.

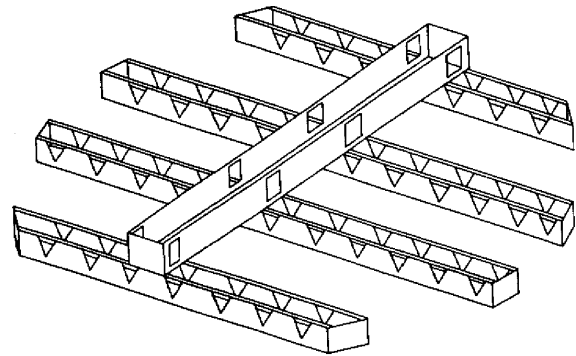


Fig. 6.24 Weir-trough liquid distributor. (The United States Stoneware Company.)

So some sort of device to distribute the flow over the entire cross section of the tower is needed. This device is called a **distributor**.

Even if the flow is evenly distributed at the top of tower, channeling might still develop as the fluid trickles down. When two thin films converge they tend to form a thick film and a dry patch, which results in a reduction in contact area. So **redistributors** are placed every 10-15 feet along the length of the tower.

A TYPICAL ABSORBER DESIGN PROBLEM

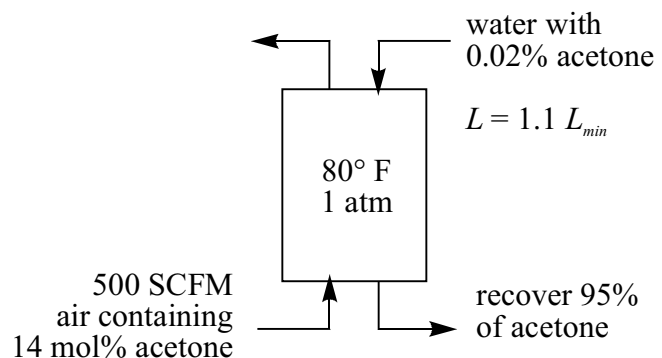
To motivate the next few lectures, let's pose a typical design problem. For this example, I'm going to take Prob. 22-1 from McCabe, Smith & Harriott.

Problem: treat 500 SCFM of air containing 14 mol% acetone to remove 95% of the acetone by absorption in liquid water in a packed bed operating at 80°F and 1 atm, with 1-inch raschig rings. The feed water contains 0.02% acetone and the flowrate is 1.1 times the minimum.

The partial pressure of acetone over an aqueous solution at 80°F can be calculated from

$$p_A = P_A^o \gamma_A x_A \quad \text{where} \quad \ln \gamma_A = 1.95(1-x)^2$$

where $P_A^o = 0.33$ atm is the vapor pressure of acetone at 80°F. As the designer, you must select the following:



- flowrate of water
- diameter of tower
- height of packing

Solution Overview:

Choice of liquid flowrate: $L = 1.1$ to 1.5 times L_{\min}

Just as with distillation, there is a minimum L/V required to achieve the desired separation. In typical operation of an absorber, the liquid rate is chosen to be just above the minimum.

Tower diameter: $\frac{\Delta p}{Z_T} = 0.25$ to $0.5 \frac{\text{inch H}_2\text{O}}{\text{ft of packing}}$

The diameter of the tower is usually chosen on the basis of pressure drop. Generally, for a particular L and V , the smaller the column diameter, the larger the mass velocities will be, and the larger the pressure drop. Generally, large mass velocities are desirable because they give high mass transfer coefficients, but too large mass velocities cause "flooding" which severely decreases mass transfer rates. The pressure drop above is about optimum.

Tower height:
$$Z_T = \frac{V/S}{\underbrace{K_y a}_{H_{Oy}}} \underbrace{\int_{y_a}^{y_b} \frac{dy}{y - y^*}}_{N_{Oy}}$$

The height of the tower is determined by mass transfer rates. Basically, the gas and liquid phases need to be in contact for a certain time for the acetone to diffuse from the gas phase into the liquid. The equation above is called the "design equation".

$$H_{Oy} \equiv \frac{V/S}{K_y a}$$

is called the ***height of one transfer unit***, where $K_y a$ is the overall mass transfer coefficient times the interfacial area per unit volume of packing, and

$$N_{Oy} \equiv \int_{y_a}^{y_b} \frac{dy}{y - y^*}$$

is called the ***number of transfer units***,* where y is the mole fraction of the transferable component and $y - y^*$ is the local driving force for mass transfer.

* This particular formula is for dilute solutions, which is probably not really applicable to the current example, but it is applicable in the homework problems.

Detailed Solution:

First of all, what is “SCFM”? This stands for “standard cubic feet per minute”

SCFM = standard (0°C, 1 atm) cubic feet per minute

where “standard” means that the volume is evaluated at standard conditions. We can convert SCFM into moles. Starting with the ideal gas law,

$$PV = nRT$$

or

$$\frac{V}{n} = \frac{RT}{P} = \frac{R(273^\circ K)}{(1 atm)} = 22.4 \frac{\text{liters}}{\text{gmol}} = 359 \frac{\text{ft}^3}{\text{lbmol}}$$

depending of which set of units are used to express R . Recall that a gmol is the quantity of material whose mass equals the molecular weight in grams. Similarly, a lbmol is the quantity of material whose mass equals the molecular weight in pounds. For example, air has a molecular weight of 29:

$$MW \text{ of air} = 29 \frac{\text{g}}{\text{gmol}} = 29 \frac{\text{lb}}{\text{lbmol}}$$

Thus we can convert 500 SCFM into a molar flowrate:

$$\frac{500 \text{ ft}^3/\text{min}}{359 \text{ ft}^3/\text{lbmol}} = 1.39 \frac{\text{lbmol}}{\text{min}} = V$$

Now let's move on to determine the liquid flowrate required. Recall that in distillation the slope of the ROL is given by

$$\text{slope of ROL} = \frac{L}{V} = \frac{R}{R+1}$$

You should also recall that there exists a minimum value of the reflux ratio for any given combination of product and feed specifications. This minimum value of R translates into a minimum allowable L/V . There is a similar minimum L/V for gas absorption. To find the minimum reflux ratio in distillation, we needed to plot an operating line and an equilibrium curve.

EQUILIBRIUM CURVE

In Prob. 22-1, McCabe gives us equilibrium data in the form of partial pressure of acetone in the gas phase, p_A , as a function of the mole fraction of acetone in the liquid, x :

$$P_A = P_A^o \gamma_A x \quad (109)$$

$$P_A^o = \text{vapor pressure of acetone at } 80^\circ\text{F} = 0.33 \text{ atm}$$

$$\gamma_A = \text{activity coefficient for liquid mixture}$$

Activity coefficient is a measure of nonideality of the liquid phase. For *ideal solutions* the activity coefficient is unity:

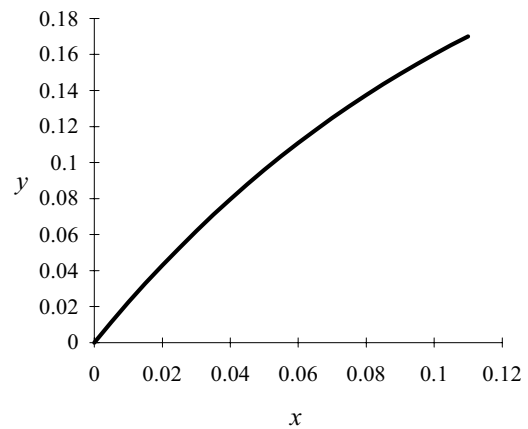
$$\gamma_A = 1 \text{ (ideal solution)}$$

For ideal solutions, (109) reduces to Raoult's law. Our solution of acetone in water is not ideal, but McCabe kindly gives us a model

$$\ln \gamma_A = 1.95(1-x)^2$$

Note that $\gamma_A \rightarrow 1$ (i.e. $\ln \gamma_A \rightarrow 0$) as $x \rightarrow 1$. This is a general rule: pure components also behave ideally since nonideal behavior results from interactions between different molecules; there are no different molecules when the fluid is pure. We can obtain an expression for the mole fraction of acetone in the gas just by dividing the partial pressure by the total pressure:

$$y = \frac{P_A}{P}$$



where we use $P = 1 \text{ atm}$. Repeating this for different x 's to obtain y 's up to 0.14 (the feed concentration), we obtain the curve at right, where

$x = \text{mole fraction of acetone in the liquid (2}^{\text{nd}} \text{ component is water)}$

$y = \text{mole fraction of acetone in the gas (2}^{\text{nd}} \text{ component is air)}$

OPERATING LINE

Suppose we are trying to absorb acetone from a mixture of air and acetone by contacting the air mixture with water. Let

$L, V =$ total molar flowrates

$x, y =$ mol.frac. of transf. comp.

where the transferrable component is acetone in this example. Performing a component balance on the transferrable component about the top section of the tower yields:

$$L_a x_a + Vy = Lx + V_a y_a \quad (110)$$

Solving for y :

$$y = \frac{L}{V}x + \frac{V_a y_a - L_a x_a}{V}$$

This relationship $y(x)$ between the mole fractions in the liquid and gas streams is again known as the **operating line**, since the relationship is imposed by a component mole balance. However as acetone is transferred from the gas to liquid, L and V change. In particular, their ratio changes. Thus the operating line is not straight. This makes it difficult to determine the minimum water flowrate

There are two limiting cases where we can easily predict the change in L and V .

Approx. #1: Only One Transferable Component

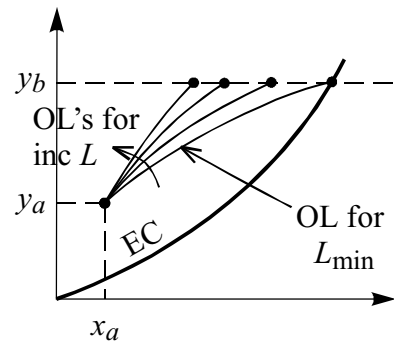
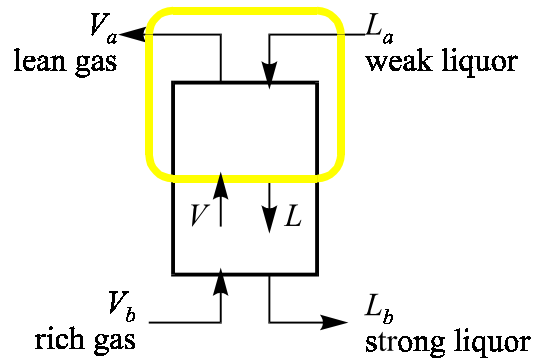
It is often possible to assume that only one component is undergoing transfer between the liquid and gas streams. For example, in our problem acetone is being transferred from the air to the water:

transferable: acetone

non-transferable: air, water

Although some of the water will evaporate when it contacts the air and some of the air will dissolve in the water, the molar rates of transfer of these components can often (but not always) be neglected compared to rate of acetone transfer. When you can neglect the molar transfer rate of all but one component, then significant simplification can be made. If we can neglect evaporation of water and dissolution of air, then the moles of water (the nontransferable component) in the liquid stream must be the same at all elevations:

$$(1-x)L \equiv L' = \text{const} \quad \text{so} \quad L = \frac{L'}{1-x} \quad (111)$$



Similarly, the moles of air in the gas stream must be the same at all elevations:

$$(1-y)V \equiv V' = \text{const} \quad \text{so} \quad V = \frac{V'}{1-y} \quad (112)$$

(111) and (112) into (110):

$$\frac{L'x_a}{1-x_a} + \frac{V'y}{1-y} = \frac{L'x}{1-x} + \frac{V'y_a}{1-y_a}$$

where L', V' are constants. If we now express concentrations in terms of *mole ratios* instead of mole fraction:

$$X \equiv \frac{x}{1-x} = \frac{\text{moles of A in liquid}}{\text{moles of non-A in liquid}}$$

$$Y \equiv \frac{y}{1-y} = \frac{\text{moles of A in gas}}{\text{moles of non-A in gas}}$$

then this equation becomes very simple:

$$L'X_a + V'Y = L'X + V'Y_a$$

or

$$Y = \frac{L'}{V'}X + \left(Y_a - \frac{L'}{V'}X_a \right) \quad (113)$$

Since $L'/V' = \text{const}$, this is the equation of a straight line. Thus for the special case of one-transferable component, the operating line is straight on mole ratio coordinates. Note that mole ratios need not be smaller than unity:

$$0 \leq x \leq 1$$

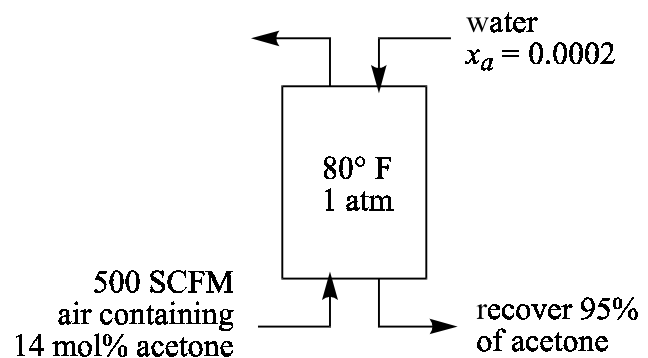
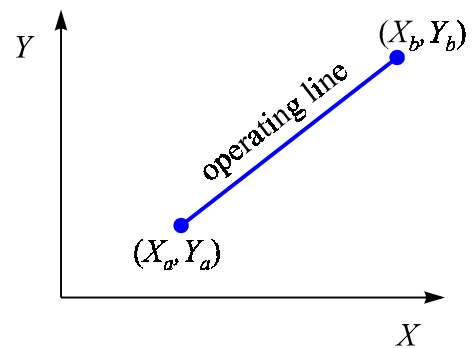
but

$$0 \leq X \leq \infty$$

although they are in this example.

Let's apply this "one transferable component" approximation to Prob. 22-1. One point on the operating line is (X_a, Y_a) . We are told that the inlet water contains a small amount of acetone:

$$x_a = 0.0002 \rightarrow X_a = \frac{x_a}{1-x_a} = 0.0002$$



The concentration of acetone in the gas phase is determined from the specification that we want to remove 95% of the acetone from the feed:

$$y_a V_a = 0.05 y_b V_b$$

$$y_a \frac{V'}{1-y_a} = 0.05 y_b \frac{V'}{1-y_b}$$

Since V' (the molar air flowrate) is the same at either end of the column, we can cancel it out, leaving

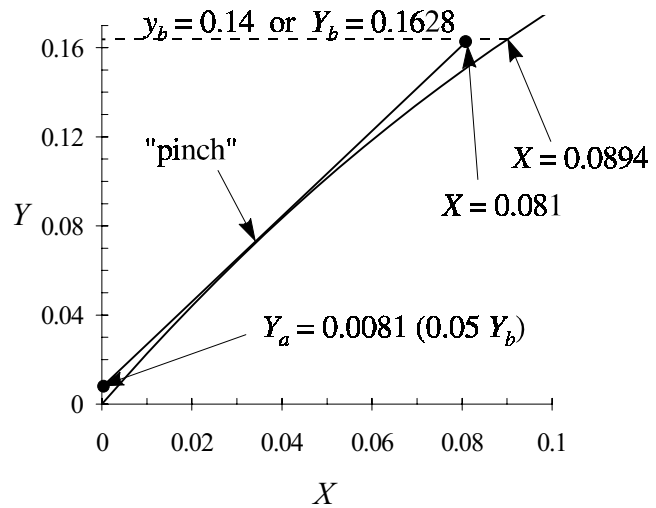
$$Y_a = 0.05 \underbrace{Y_b}_{\frac{0.14}{1-0.14}} = 0.00814$$

The second point on the operating line must lie somewhere along the line

$$Y = Y_b = 0.1628$$

When you plot this up, you find that the equilibrium curve is below the operating line. This is generally true for gas absorption and makes sense when you realize that the gas must be richer in the ammonia than at equilibrium — otherwise the acetone would not spontaneously absorb into the liquid.

Note that there is a minimum slope which the operating line can have before a “pinch” develops with the equilibrium curve. This minimum slope represents the minimum value of



$$\left(\frac{L'}{V'}\right)_{\min} = \frac{0.1628 - 0.00814}{0.081 - 0.0002} = 1.91$$

$$L'_{\min} = 1.91 V' = 1.91 \times 1.39 \frac{\text{lbmol}}{\text{min}} = 2.66 \frac{\text{lbmol}}{\text{min}}$$

Multiplying this by the molecular weight of water (18 lb/lbmol) and dividing by the density of water (8.33 lb/gal) yields a minimum water flowrate of 5.75 gal/min.

Approx. #2: Dilute Solution

In other problems, the solutions might be very dilute. If the solutions are sufficiently dilute, then mole ratios are virtually equal to mole fraction:

if $x \ll 1$

then $1-x \approx 1$

and $X \equiv \frac{x}{1-x} \approx x$

When this is also true for the gas stream, then (113) can be approximated as

$$y = \frac{L'}{V'}x + \left(y_a - \frac{L'}{V'}x_a \right)$$

In fact, we can also drop the prime, since $L' \approx L$:

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

Thus the operating line will also be linear on mole fraction coordinates if the solutions are sufficiently dilute. This linear operating line on mole fraction coordinates will also apply even if we have more than one transferrable component, provided *both phases are sufficiently dilute in all the transferrable components*.

INTERFACIAL MASS TRANSFER: REVIEW

An important design parameter is the depth of packing required. In distillation, the tower height was determined by the number of plates required times the plate separation (which is usually 1-2 feet). The number of plates required for a given separation is determined by the operating and equilibrium lines. For packed towers, the height also depends on the operating and equilibrium lines, but in addition it is inversely proportional to the *mass transfer coefficient*, which in distillation plays only a minor role in determining plate efficiency.

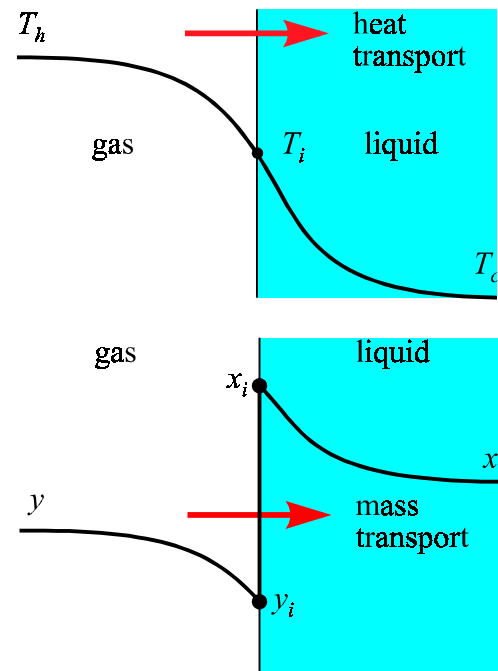
Now that we have established the importance of interfacial mass transfer in packed towers, let's talk about modelling mass transfer across a phase boundary.

Let's start by recalling the driving force for heat transfer across an interface. Suppose I contact a hot gas with a cold liquid. The temperature profile near the interface will look something like that show at right. There are two characteristics of this sketch which are important:

1. heat flows from high to low temperature
2. temperature is continuous across the interface

Interfacial mass transfer is similar to interfacial heat transfer, but it is also different.

1. mass transfer occurs in the direction from high to low chemical potential (*not necessarily from high to low concentration**)
2. chemical potential is continuous across interface (concentration is generally *not* continuous)



The main difference is evident in the sketch of the concentration profile near the interface. Note the *discontinuity in the mole fraction at the interface*.*

$$y_i \neq x_i$$

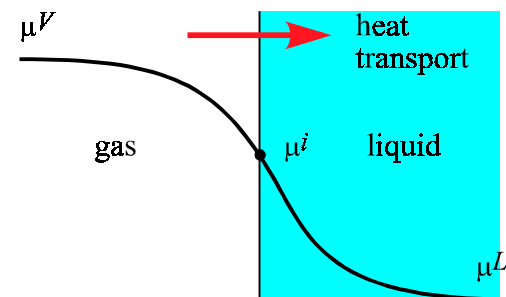
$$T_{yi} = T_{xi} = T_i$$

The reason for this discontinuity in concentration across the interface has to do with thermodynamic criteria for phase equilibrium. Recall:

phase equilibrium: $\mu_j^V = \mu_j^L$ for $j=1, \dots, N_c$

thermal equilibrium: $T^V = T^L$

where μ_j is called the **chemical potential** which plays the role of temperature in mass transfer. Unfortunately, there exists no “thermometer” for measuring chemical potential. Instead, we are forced to measure chemical concentration. While chemical potential usually



* Within a single phase, transport is usually from high to low concentration.

* Instead of component i , the subscript “ i ” will be used to denote quantities evaluated at the interface between two phases. In place of i , we will use j to denote components.

increases with concentration within any given phase (this is why diffusion of a solute occurs from high to low concentration), when comparing chemical potentials between two phases, there is no general correlation between chemical potential and concentration.

To illustrate this, recall the simplest case of VLE: an ideal gas mixture in equilibrium with an ideal solution. This leads to Raoult's law:

$$y_j P = x_j P_j^o$$

Note that:

$$\frac{y_j}{x_j} = \frac{P_j^o}{P} \neq 1$$

Thus

$$y_j \neq x_j$$

for VLE

even in the simplest case of vapor-liquid equilibrium, the mole fractions are not equal, except in the trivial case when you have only one component and the total pressure is the vapor pressure.

Definitions of Transfer Coefficients

Recall from the first part of this course, the local heat flux through the interface can be related to the local temperatures using any one of three types of local heat transfer coefficients:

$$\frac{\text{rate of heat transfer}}{\text{interfacial area}} = h_x(T_h - T_i) = h_y(T_i - T_c) = U(T_h - T_c) \quad (114)$$

where

$$h_x, h_y = \text{one-phase local heat transfer coefficients}$$

$$U = \text{overall local coefficient.}$$

Basically these equations say that the rate of heat transfer is proportional to the driving force (which is the departure from equilibrium) and the proportionality constant is the heat transfer coefficient.

Similar definitions of transport coefficients can be made for mass transfer:

$$\frac{\text{molar rate of transfer}}{\text{interfacial area}} = k_x(x_i - x) = k_y(y - y_i) = K_x(x^* - x) = K_y(y - y^*) \quad (115)$$

where

$$k_x, k_y = \text{one-phase local mass transfer coefficients}$$

$$K_x, K_y = \text{overall local mass transfer coefficients}$$

Comparing the mass transport expressions in (115) with their heat-transfer analogues in (114), there is a good deal of similarity — especially in the one-phase relations. For a single phase, the

driving force is the difference between the concentration or temperature in the bulk and in the concentration or temperature at the interface.

But the driving force for the overall coefficients look a little different. The overall driving force for heat transfer is just the difference between the temperature of the hot and cold fluid

$$T_h - T_c$$

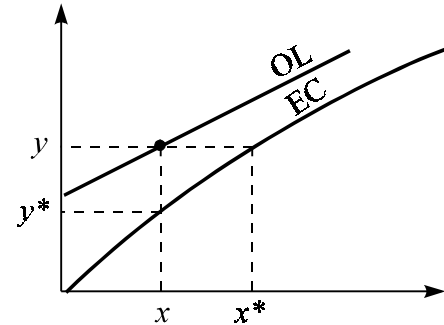
By simple analogy, you might expect the overall driving force for mass transfer to be the difference in concentration of the two phases:

$$y - x \neq \text{overall driving force}$$

Instead

$$y - y^* \text{ and } x^* - x$$

appear in (115) as the overall driving force. The *'s are defined as shown on the figure at right. Basically $y - y^*$ and $x^* - x$ are two different measures of the distance between the operating line and the equilibrium curve at that elevation in the packed bed where the liquid and gas concentrations are (x,y) .

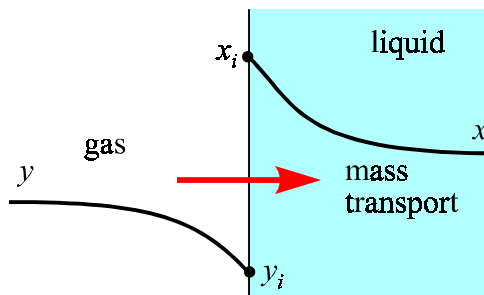


$x-y$ does not represent the overall driving force for mass transfer, because the transport rate does not go to zero when $x-y = 0$. The transport rate is zero only at equilibrium, and $x-y \neq 0$ at equilibrium.

Determining the Interfacial Concentrations: (x_i, y_i)

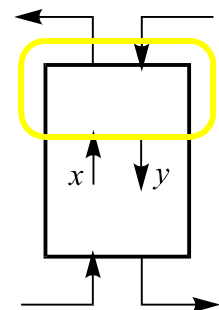
Although overall mass-transfer coefficients are the most easy to use in design, correlations are sometimes more available in the form of single-phase coefficients. We may have a need to calculate overall coefficients from the single-phase coefficients. For example, in Prob. 22-1 we are given the values of H_x and H_y . If we had instead the value of H_{Oy} we could use the value of N_{Oy} we computed last time to calculate the height of packing. In what follows, we derive a relationship among H_{Oy} , H_x and H_y .

Consider once again, the rate of interfacial transport at some arbitrary elevation in the absorber, denoted by the dotted line in the figure at right.



The profile of concentration of the transferable component near the interface at this location in the absorber looks like the sketch below at left.

At steady state, the flux of ammonia through the gas film must equal the flux of ammonia through the liquid



film:

$$N_A = k_x(x_i - x) = k_y(y - y_i) \quad (116)$$

If the fluxes were not equal, we would have ammonia building up at the interface. We will denote this interfacial flux by N_A .

Suppose the bulk compositions — x, y — are known, together with the two single-phase mass transfer coefficients. To determine the flux, we must also determine the interfacial compositions — x_i, y_i . Think of these two interfacial concentrations as two unknowns. We need two equations. One equation is provided by the requirement that (x_i, y_i) must lie on the equilibrium curve. The second relation is (116), which can be re-written as a linear relationship between y_i and x_i :

$$y_i = \underbrace{-\frac{k_x}{k_y} x_i}_{\text{slope}} + \underbrace{y + \frac{k_x}{k_y} x}_{\text{intercept}} \quad (117)$$

The intersection of (117) and the equilibrium curve gives the interfacial concentrations.

Example: In Prob. 22-1, we are given values of the heights of both single-phase coefficients (H_x and H_y) and need to evaluate the height of the overall gas-phase coefficient (H_{Oy}).

Solution: Consider the following problem:

Given: k_x and k_y

Find: K_y

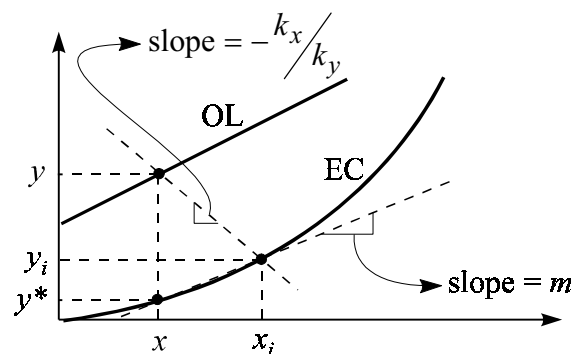
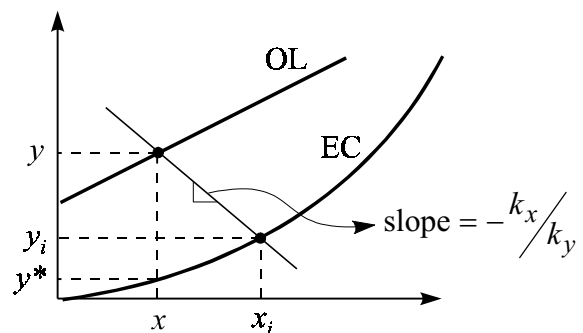
Using the definitions of the k 's and of K_y ,

$$N_A = k_x(x_i - x) = k_y(y - y_i) = K_y(y - y^*) \quad (118)$$

The relationship among the concentrations is shown in the figure at right. Adding and subtracting y_i from the overall driving force $y - y^*$:

$$\underbrace{\frac{y - y^*}{K_y}} = \underbrace{\frac{y - y_i}{K_y}} + \underbrace{\frac{y_i - y^*}{K_y}} \quad (119)$$

Using (118) we can assign meaning to two of the three differences appear above, leaving:



$$\frac{N_A}{K_y} = \frac{N_A}{k_y} + \underbrace{y_i - y^*}_{(x_i - x)m} \quad (120)$$

The remaining difference $y_i - y^*$ can be related to $x_i - x$ and the local slope of the equilibrium curve m :

$$y_i - y^* = (x_i - x)m = \frac{N_A}{k_x}m \quad (121)$$

In the second equality above, $x_i - x$ is expressed in term of the remaining single-phase mass transfer coefficient using (116). Substituting (121) into (120) and dividing by N_A :

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{m}{k_x} \quad (122)$$

where $m = \frac{y_i - y^*}{x_i - x} = \text{avg. slope of E.C.}$

Of course, if the equilibrium curve is straight (as it will be in dilute solutions), then m is its slope. This is similar to the expression for overall heat transfer coefficients for a double-pipe heat exchanger:

$$\frac{1}{U} = \frac{1}{h_x} + \frac{1}{h_y} \quad (123)$$

We said that $1/U$ represented the total resistance to heat transfer through the two phases, which is just the sum of the resistances of each phase. The main difference between (122) and (123) is the appearance of m in (122). For heat transfer, the slope of the equilibrium line is unity ($m = 1$) because at thermal equilibrium $T_y = m T_x = T_x$.

In short, (122) states that the total resistance to mass transfer equals the sum of the resistances of the gas and liquid phases. We could also have showed, in a similar fashion, that

$$\frac{1}{K_x} = \frac{1}{mk_y} + \frac{1}{k_x} \quad (124)$$

where now:

$$m = \frac{y - y_i}{x^* - x_i}$$

If the operating line is straight, these two slopes would be the same and we could relate the two overall mass transfer coefficient:

straight E.C.:

$$\frac{1}{K_y} = \frac{m}{K_x}$$

Equimolar Counter-Diffusion vs. Diffusion through Stagnant Fluid

In the form most analogous to Fourier's law of heat conduction, **Fick's law** of diffusion of a binary mixture of components A and B, the flux (moles/area/time) of component A in the +z direction is given by

$$J_{Az}^* = -D_{AB} \frac{dc_A}{dz}$$

where c_A is the molar concentration of component A and D_{AB} is the diffusion coefficient. This gives the flux of A relative to a reference frame which moves with the mole-average velocity (i.e. the average of the species velocity of each component) of the mixture (A+B). More useful in calculations is the molar flux of A relative to a stationary reference frame is

$$N_{Az} = \underbrace{-D_{AB} \frac{dc_A}{dz}}_{J_{Az}^*} + \underbrace{\frac{N_{Az} + N_{Bz}}{c}}_{\bar{v} = \text{mol average velocity}} c_A \quad (125)$$

where $c = c_A + c_B$ is the total molar concentration.

Case I: If we use a capillary tube to connect two gas reservoirs having the same total pressure but different amounts of gases A and B (see Fig. 6.2-1), we will obtain **equimolar counter-diffusion** of A and B (i.e. $N_{Az} = -N_{Bz}$). In this way, the mole-average velocity $\bar{v} = 0$ and the total pressure in both reservoirs remains constant. For $N_{Az} = -N_{Bz}$, (125) gives

$$N_{Az} = -D_{AB} \frac{dc_A}{dz} = J_{Az}^* \quad (126)$$

Case II: If instead, we have diffusion of benzene vapor above its liquid through air (which is virtually insoluble in the liquid), the air must remain stagnant (i.e. $N_{Bz} = 0$) since it cannot enter the liquid (see Fig. 6.2-2a). This is diffusion of A through stagnant B. For $N_{Bz} = 0$, (125) gives

$$N_{Az} = -D_{AB} \frac{dc_A}{dz} + N_{Az} \frac{c_A}{c} \quad \text{or} \quad (1 - y_A) N_{Az} = \underbrace{-D_{AB} \frac{dc_A}{dz}}_{J_{Az}^*}$$

Finally we have

$$N_{Az} = \frac{J_{Az}^*}{1 - y_A} \quad (127)$$

For the same driving force (concentration gradient), J_{Az}^* is the same for both cases, but N_{Az} are different. Since $1-y_A$ is always less than one, we see that equimolar counter-diffusion (126) is slower than diffusion through a stagnant fluid (127). This can be qualitatively understood as follows. Suppose that to get to class, you need to walk down a corridor that's crowded with other students. If everyone else was standing almost still (stagnant fluid), it would be easier to walk around them than if everyone is walking toward you (counter diffusion).

All of the flux expressions above apply locally at every point in the fluid. For 1-D steady equimolar counter-diffusion (from a reservoir having c_{A1} to a second reservoir having c_{A2}), (126) integrates to

$$N_{Az} = J_{Az}^* = \frac{D_{AB}}{z_2 - z_1} (c_{A1} - c_{A2}) = \frac{cD_{AB}}{z_2 - z_1} (y_{A1} - y_{A2}) = k'_y (y_{A1} - y_{A2}) \quad (128)$$

where $z_2 - z_1$ is the length of the capillary through which diffusion is occurring and k'_y is the single-phase (gas) mass transfer coefficient to be used with mole fractions and equimolar-counter diffusion. The analogous expression for diffusion through stagnant film of B is (see Section 6.2C):

$$N_{Az} = \frac{cD_{AB}}{(z_2 - z_1)(1 - y_A)_M} (y_{A1} - y_{A2}) = k_y (y_{A1} - y_{A2}) \quad (129)$$

where

$$(1 - y_A)_M = \frac{(1 - y_A)_1 - (1 - y_A)_2}{\ln \frac{(1 - y_A)_1}{(1 - y_A)_2}}$$

is the log-mean of y_B evaluated at either end of the diffusion path. Comparing (128) and (129), we see that

$$k_y = \frac{k'_y}{(1 - y_A)_M}$$

Similar relations exist for diffusion in the liquid phase:

$$k_x = \frac{k'_x}{(1 - x_A)_M}$$

and between the overall mass-transfer coefficients for equimolar counter-diffusion and diffusion through a stagnant film:

$$K_y = \frac{K'_y}{(1 - y_A)_{*M}} \quad \text{and} \quad K_x = \frac{K'_x}{(1 - x_A)_{*M}}$$

$$\text{where } (1 - y_A)_{*M} = \frac{(1 - y_A^*) - (1 - y_{AG})}{\ln \frac{(1 - y_A^*)}{(1 - y_{AG})}} \quad \text{and} \quad (1 - x_A)_{*M} = \frac{(1 - x_A^*) - (1 - x_{AL})}{\ln \frac{(1 - x_A^*)}{(1 - x_{AL})}}$$

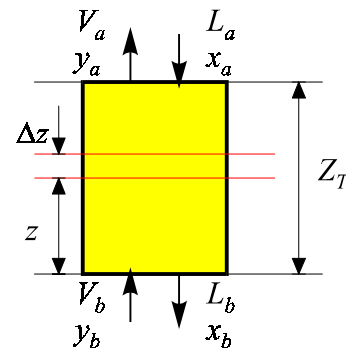
and where y_{AG} is the mole fraction in the bulk of the gas, y_A^* is the mole fraction which would be in equilibrium with the bulk liquid having a mole fraction of x_{AL} , and x_A^* is mole fraction in the bulk of the liquid which would be in equilibrium with the bulk gas having a mole fraction of y_{AG} .

HEIGHT OF A PACKED TOWER

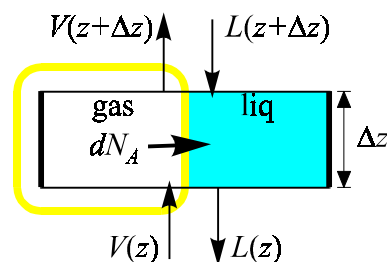
The analysis which follows has as its goal the determination of the height of packing required. The approach is similar to that used in the design of double-pipe heat exchangers in which the goal is the determination of the area of heat-exchange surface required. The main complication arises from the fact that the mass flux is not proportional to $y-x$; instead, the mass flux is proportional to $y-y^*$.

We have to chop up the tower into pieces which are small enough so that the driving force is virtually uniform throughout each piece. Since the compositions change only with z , we chop up the tower in such a way that we produce pieces which have $z \approx \text{const}$, which is a thin horizontal slice.

Now let's take a closer look at what happens inside this slice of the tower. The slice contains solid packing as well as liquid and gas streams. In what follows, we will ignore the solid and treat the liquid and gas phases as if they were completely separated, rather than interspersed in each other.



double-pipe hxr analogy:



Let's do a mass balance on the acetone in the gas phase only contained within our slice of column. Besides the liquid streams entering and leaving the slice, we have acetone crossing the

interface between the gas and liquid phases. The rate of absorption per unit area can be expressed in terms of the local overall mass transfer coefficient:

$$\frac{\text{molar rate of transfer}}{\text{interfacial area}} = K_y(y - y^*) \quad (130)$$

$$U_o(T_h - T_c)$$

We could also have used one of the other expressions in (115); this one proves later to be more convenient than some of the others.

Just like the overall heat transfer coefficient U_o depends on the flowrates of both fluids being contacted in the heat exchanger, the overall mass transfer coefficient K_y depends on both flowrates

$$K_y = K_y(L, V)$$

To obtain the rate of transfer across the interface in our slice of column, we need to multiply (130) by the *interfacial area* in that slice.

In a heat exchanger, the heat transfer surface is fixed by the geometry of the equipment selected: it is just the area of the pipe wall or the tubes. In particular, the heat transfer area does not depend on the flowrates of the hot and cold streams. On the other hand, the boundary between liquid and gas in a packed bed is very complex and very hard to measure directly. Most importantly, the area also depends on the flowrates of the gas and liquid streams (L, V).

The interfacial area is usually expressed as a , the interfacial area per unit volume of packing:

$$\frac{\text{interfacial area}}{\text{volume of packing}} \equiv a = a(L, V) \quad (131)$$

$$\frac{\pi D_o dz}{\pi (D_o/2)^2 dz} = \frac{4}{D_o}$$

One empirical correlation relating area to flowrates is the *Schulman Correlation* (Table 6.3 of Treybal):

$$a = m G_x^\alpha G_y^\beta$$

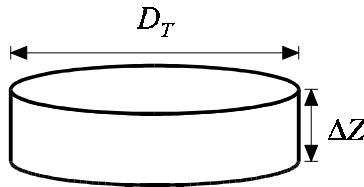
where G_x and G_y are the mass flowrates of the liquid or gas stream divided by the cross-sectional area of the tower

$$G \equiv \frac{\text{mass/time}}{\pi D^2/4} = \text{mass velocity}$$

and where m , α , β are constants which depend on the type and size of packing used. Multiplying (130) by (131):

$$\frac{\text{rate of transfer}}{\text{interf area}} \times \frac{\text{interf area}}{\text{vol. of packing}} = K_y (y - y^*) \times a$$

$$r \equiv \frac{\text{molar rate of transfer}}{\text{volume of packing}} = K_y a (y - y^*) \quad (132)$$



If we now multiply by the volume of this slice of the packed column, we will obtain the rate at which acetone crosses the interface in this slice:

$$\text{rate of transfer} = r S \Delta z = dN_A$$

where $S = \text{empty tower cross-section} = \frac{\pi D_T^2}{4}$

$$S \Delta z = \text{volume of slice}$$

At steady state, the rate of transport of acetone into the vapor must equal the rate out:

$$\text{in} = \text{out}$$

$$(Vy)|_z = (Vy)|_{z+\Delta z} + rS\Delta z \quad (133)$$

Dividing by $-\Delta z$ and letting $\Delta z \rightarrow 0$, (133) becomes:

$$\frac{d(Vy)}{dz} = -rS \quad (134)$$

$$\frac{4U_o}{D_o} (T_h - T_c)$$

$$dq = U_o \frac{dA_o}{\pi D_o dz} (T_h - T_c)$$

$$\dot{m} \rho c_p T(z) = \dot{m} \rho c_p T(z + \Delta z) + dq$$

$$\dot{m} \rho c_p \frac{dT}{dz} = -\frac{dq}{dz} = \pi U_o D_o (T_h - T_c)$$

Now the total molar flowrate (V) will change as the gas phase loses acetone, but the flowrate of acetone-free air (V') does not change with Z :

$$V = \frac{V'}{1-y} \quad \rightarrow \quad Vy = \frac{V'y}{1-y}$$

$$d(Vy) = d\left(\frac{V'y}{1-y}\right) = V' d\left(\frac{y}{1-y}\right) = \dots = V' \frac{dy}{(1-y)^2} = V \frac{dy}{1-y}$$

(134) becomes:
$$\frac{V}{1-y} \frac{dy}{dz} = -rS = -K_y a (y - y^*) S \quad (135)$$

The second equation is obtained by substituting our expression for the rate of absorption r from (132). We can now solve this equation for the height dZ of the slice:

$$dz = \frac{-Vdy}{(1-y)(y-y^*)(K_y a)S}$$

So if we know the local mole fractions y and y^* and the change in the mole fraction dy of the gas phase which occurred between the top and bottom of this slice, we can calculate the height of the slice. The total height of packing is the sum of the height of each slice:

$$Z_T = \int_0^{Z_T} dz = \int_{y_b}^{y_a} \frac{-Vdy}{(1-y)(y-y^*)(K_y a)S}$$

Factoring out the S , which is constant along the entire height of the packing, and changing the order of integration (since $y_b > y_a$):

$$Z_T = \frac{1}{S} \int_{y_a}^{y_b} \frac{Vdy}{(1-y)(y-y^*)(K_y a)}$$

Now K_y depends on G_x and G_y , which in turn depend on gas composition. For the case of a dilute gas stream, we know that

$$y \ll 1 \quad 1-y \approx 1 \quad V \approx V' = \text{const} \quad K_y a \approx \text{const}$$

After making these approximations, we have

$$Z_T = \underbrace{\frac{V}{K_y a S}}_{H_{Oy}} \underbrace{\int_{y_a}^{y_b} \frac{dy}{y-y^*}}_{N_{Oy}} \quad (136)$$

which serves as the basic design equation for packed bed absorbers.

For very dilute solutions, this integral can be evaluated analytically (i.e. numerical integration is not required). If both $x \ll 1$ and $y \ll 1$ hold, then the molar flowrates of the two streams won't change much as the solute is transferred across the phase boundary. In particular, the ratio of the flowrates will be constant:

$$\text{then} \quad L/V \approx L'/V' = \text{const}$$

This means that the operating line will be straight, even on mole fraction coordinates:

$$y = (L/V)x + [y_a - (L/V)x_a]$$

Also, for sufficiently dilute solutions, Henry's law always applies so that

$$y^* = mx$$

will also be a straight line. When both operating and equilibrium curves are straight, then the integration can be done analytically instead of numerically. The result is:

$$\text{straight OL \& EC:} \quad N_{Oy} = \frac{y_b - y_a}{\overline{(y - y^*)}_L} \quad (137)$$

where $\overline{(y - y^*)}_L$ is the log-mean of $y_b - y_b^*$ and $y_a - y_a^*$ which represent the driving force at the bottom and top of the tower, respectively.

TRANSFER UNIT

Meaning can be given to the integral. Even if the integrand varies significantly over the domain of integration, we can still pull it outside the integral, provided we replace it with some appropriate value, which can be thought of as the mean value for this range. Recall the **Mean Value Theorem** of Calculus:

$$\int_{y_a}^{y_b} \frac{dy}{y - y^*} = \frac{1}{(y - y^*)_{\text{avg}}} \int_{y_a}^{y_b} dy = \frac{y_b - y_a}{(y - y^*)_{\text{avg}}} \quad (138)$$

Of course, it is not usually known what type of average to use, but for the present purpose, the precise value is not important. The integral can be thought of as the total change in gas mole fraction divided by the average driving force.

(Gas Phase) **Transfer Unit** -- a slice (not necessarily thin) of an absorber in which the gas undergoes a change in y equal to $(y - y^*)_{\text{avg}}$ which represents the average driving force over the entire absorber.

No. of TU's -- the number of these it takes to make the entire absorber (not necessarily an integer)

Height of TU -- height of a slice of an absorber corresponding to one TU

From (138), we see that the integral clearly represents the number of transfer units:

$$N_{Oy} = \int_{y_a}^{y_b} \frac{dy}{y - y^*} \quad (139)$$

This is called the number of **overall gas phase transfer units** since it is based on the overall driving force expressed as the gas-phase mole fraction. Since the product in (136) represents the total height of packing, the coefficient of this integral must represent the **height of a transfer unit**:

$$H_{Oy} = \left(\frac{V/S}{K_y a} \right)_{\text{avg}}$$

So that our design equation can be rewritten as:

$$Z_T = H_{Oy} N_{Oy}$$

which is called the **HTU method** for sizing an absorber. Throughout the derivation above we made use of one type of mass transfer coefficient:

$$r = K_y a (y - y^*)$$

Of course, other types of mass transfer coefficient are commonly encountered and can also be used to compute the height of packing required:

$$r = K_x a (x^* - x) = k_x (x_i - x) = k_y (y - y_i)$$

to mention a few. Of course, there are still more definitions based on driving forces expressed as differences in molar concentration or partial pressure. Any one of these mass transfer coefficients can be used in the HTU method:

$$Z_T = H_{Oy} N_{Oy} = H_{Ox} N_{Ox} = H_x N_x = H_y N_y$$

where

$$N_{Ox} = \int_{x_b}^{x_a} \frac{dx}{x^* - x} \quad H_{Ox} = \left(\frac{L/S}{K_x a} \right)_{\text{avg}}$$

$$N_x = \int_{x_b}^{x_a} \frac{dx}{x_i - x} \quad H_x = \left(\frac{L/S}{k_x a} \right)_{\text{avg}}$$

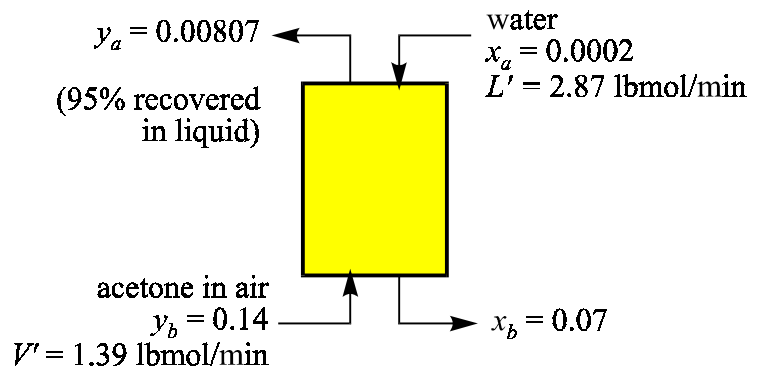
$$N_y = \int_{y_a}^{y_b} \frac{dy}{y - y_i} \quad H_y = \left(\frac{V/S}{k_y a} \right)_{\text{avg}}$$

Note that the N 's are not equal to each other; thus the number of transfer units depends on which driving force you use.

$$N_y \neq N_{Oy}$$

EVALUATION OF NTU'S

Let's see how this works by continuing the example we started a couple of lectures back (see page 141). The problem is summarized in the figure at right. We want to evaluate N_{Oy} from (139). The y in this expression is the mole fraction of acetone in the absorber at some particular elevation. If the corresponding mole fraction of acetone in the water is x , then two are related by the operating line:



$$y(x): \quad L' \left(\frac{x}{1-x} - \frac{x_a}{1-x_a} \right) = V' \left(\frac{y}{1-y} - \frac{y_a}{1-y_a} \right) \quad (140)$$

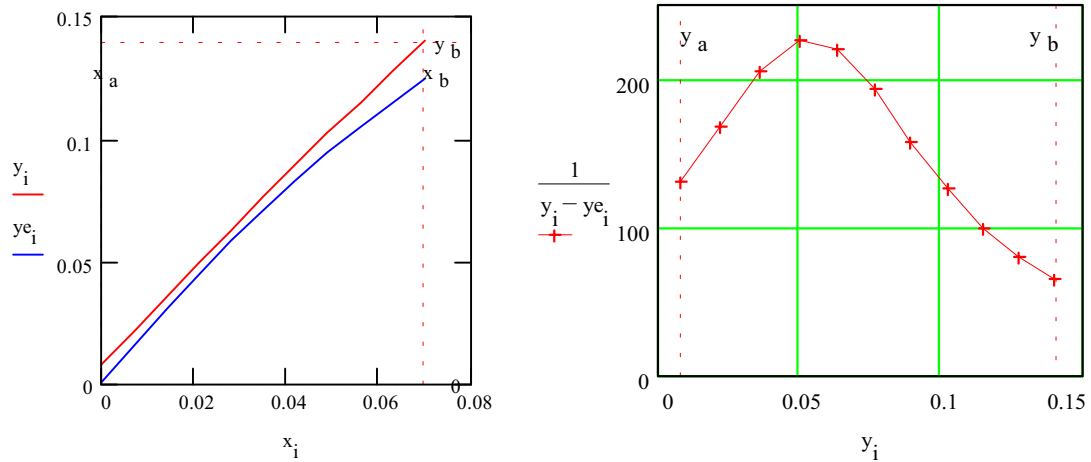
To obtain $x_b = 0.07$ (specified in problem statement) with $x_a = 0.0002$, $y_a = 0.00807$ (5% of acetone remains with gas) and $y_b = 0.14$, we find that

$$L'/V' = 2.06$$

With this ratio known, given a value of y in the interval $y_a \leq y \leq y_b$, we can use the operating line to solve for $x(y)$. On the other hand, $y^*(x)$ is the mole fraction of acetone in the gas, which would be in equilibrium with a liquid having mole fraction x .

$$y^*(x) = \frac{P_{ace}}{P} = \frac{P'_{ace}}{P} \gamma x = 0.33 \exp[1.95(1-x)^2] x \quad (141)$$

A plot of $y(x)$ and $y^*(x)$ is shown below at left. Neither curve is a straight line on these



coordinates, although the operating line is close.

To evaluate the integral, we need to compute the integrand at various points in the domain:

y	x from (140)	y^* from (141)	$\frac{1}{y - y^*}$
$y_a = 8.07E-03$	$2.00E-04$	$4.64E-04$	131.401
0.022	$7.18E-03$	0.016	168.635
0.036	0.014	0.031	204.747
0.05	0.021	0.045	225.474
0.063	0.028	0.059	219.902
0.076	0.035	0.071	192.77
0.089	0.042	0.083	158.147
0.102	0.049	0.094	126.193
0.115	0.056	0.105	100.38
0.128	0.063	0.115	80.583
$y_b = 0.14$	0.07	0.125	65.615

A plot of the integrand might look something like that shown above at right. The area under this curve represents N_{Oy} .

$$N_{Oy} = \int_{y_a}^{y_b} \frac{dy}{y - y^*} = 21.0$$

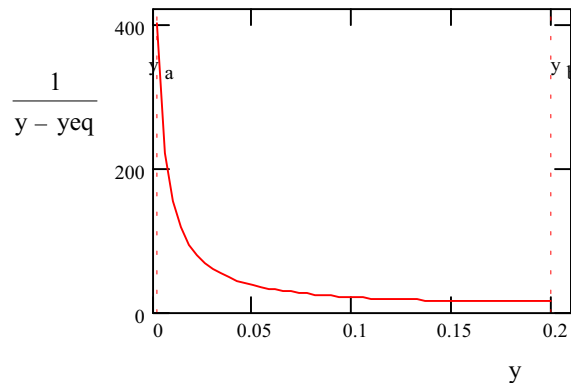
To evaluate this integral in Mathcad, it is convenient to pose y and y^* as functions of x : $y(x)$ is the operating line given by (140) and $y^*(x)$ is the equilibrium curve given by (141). Then

$$N_{Oy} = \int_{y_a}^{y_b} \frac{dy}{y - y^*} \stackrel{dy = \frac{dy}{dx} dx = y'(x) dx}{=} \int_{x_a}^{x_b} \frac{y'(x)}{y(x) - y^*(x)} dx = 21.0$$

The maximum value of the integrand occurred at the point in the column where the operating line comes closest to the equilibrium curve. The denominator $y - y^*$ is a measure of this distance. Because the equilibrium curve turns downward in this case, the "pinch" point occurs in the middle of the range. In other cases (e.g. NH_3 in water), the equilibrium curve turns upward instead.

Special Case: $y_a \ll 1$ with concave downward EC.

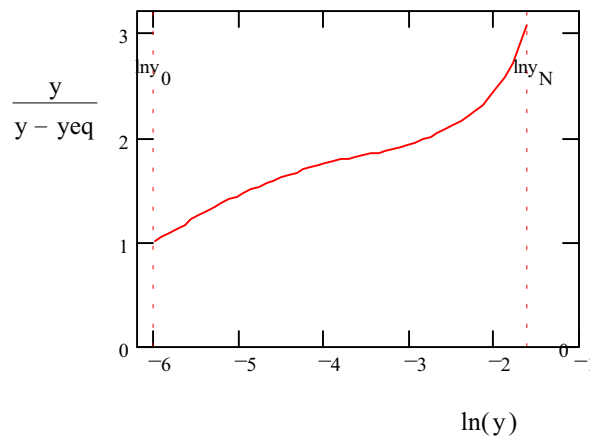
The figure at right shows a similar plot you will obtain for Prob. 22.2 on the Homework. In this case, the denominator of the integrand becomes very small near the lower limit; thus the integral has much of its area under a "spike" located at the lower limit.



To integrate such a function accurately, you will need a very small grid spacing — which means a lot of points — or at least very small spacing under the spike — which means a nonuniform grid. One solution is to transform the integral by multiplying and dividing the integrand by y :

$$N_{Oy} = \int_{y_a}^{y_b} \frac{dy}{y - y^*} = \int_{y_a}^{y_b} \frac{y}{y - y^*} \times \frac{dy}{y} = \int_{y_a}^{y_b} \frac{y}{y - y^*} d \ln y$$

Thus we plot $y/(y - y^*)$ versus $\ln y$. Since both the numerator and the denominator become small at the lower limit, the quotient tends to be more near constant with y , allowing the integration to be done with fewer points and a uniformly spaced grid.



ANALOGY WITH DOUBLE-PIPE HXER

Comparing (137) with (138), we see that for very dilute solutions, the average driving force is the log-mean. This result is quite analogous to our design equation for double-

pipe heat exchangers. To see this analogy, let's compute the total rate of ammonia transfer over the entire packed tower:

$$q_T = V(y_b - y_a) \quad (142)$$

Recall the design equation:
$$Z_T = H_{Oy} N_{Oy} = \frac{V/S}{K_y a} \frac{y_b - y_a}{\overline{(y - y^*)}_L} \quad (143)$$

This contains the product that appears in (142). Solving (143) for $V(y_b - y_a)$

$$V(y_b - y_a) = K_y a \underbrace{SZ_T}_{\text{total volume of packing}} \overline{(y - y^*)}_L$$

where SZ_T is the total volume of packing in the absorber and a is the interfacial area per unit volume of packing. Thus

$$aSZ_T = \text{total interfacial area in entire absorber} \equiv A_T$$

and substituting in (142) yields:

$$q_T = K_y A_T \overline{(y - y^*)}_L$$

which is analogous to:

$$q_T = UA_T \Delta T_L$$

Thus, for dilute solutions, the design equation for an absorber is identical in form to that for heat exchangers: with the overall mass transfer coefficient K_y analogous to the overall heat transfer coefficient U and the log-mean of $y - y^*$ at the two ends of the absorber analogous to the log-mean ΔT .

RELATIONSHIPS AMONG H_{Ox} , H_{Oy} , H_x AND H_y

In (122) on page 153, we obtained a relationship between the overall mass-transfer coefficient and the single-phase mass-transfer coefficients. This relationship can be easily modified to relate the corresponding heights of transfer units.

Dividing both sides of (122) by a (the interfacial area per volume of packing), we obtain:

$$\frac{1}{K_y a} = \frac{1}{k_y a} + \frac{m}{k_x a} \quad (144)$$

where

$$m = (y_i - y^*) / (x_i - x) = \text{avg. slope of E.C.}$$

Of course, if the equilibrium curve is straight (as it will be in dilute solutions), then m is its slope. This is similar to the expression for overall heat transfer coefficients for a double-pipe heat exchanger:

$$\frac{1}{U} = \frac{1}{h_x} + \frac{1}{h_y} \quad (145)$$

We said that $1/U$ represented the total resistance to heat transfer through the two phases, which is just the sum of the resistances of each phase. The main difference between (144) and (145) is the appearance of m in (144). For heat transfer, the slope of the equilibrium line is unity ($m = 1$) because at thermal equilibrium $T_y = m T_x = T_x$.

In short, (144) states that the total resistance to mass transfer equals the sum of the resistances of the gas and liquid phases. Using (124), we could also have showed, in a similar fashion, that

$$\frac{1}{K_x a} = \frac{1}{m k_y a} + \frac{1}{k_x a}$$

where now:

$$m = (y - y_i) / (x^* - x_i)$$

If the operating line is straight, these two slopes would be the same and we could relate the two overall mass transfer coefficient:

straight E.C.:

$$1/K_y = m/K_x$$

If we now multiply (144) by V/S we have the height on an overall gas transfer unit on the left-hand side:

$$\frac{V/S}{K_y a} = \frac{V/S}{k_y a} + \frac{mV/S}{k_x a} = \frac{V/S}{k_y a} + m \frac{V}{L} \frac{L/S}{k_x a}$$

$\underbrace{\hspace{1.5cm}}_{H_{Oy}} \qquad \underbrace{\hspace{1.5cm}}_{H_y} \qquad \underbrace{\hspace{1.5cm}}_{H_x}$

Recalling the definitions for various heights of a transfer unit we end up with

$$H_{Oy} = H_y + m \frac{V}{L} H_x$$

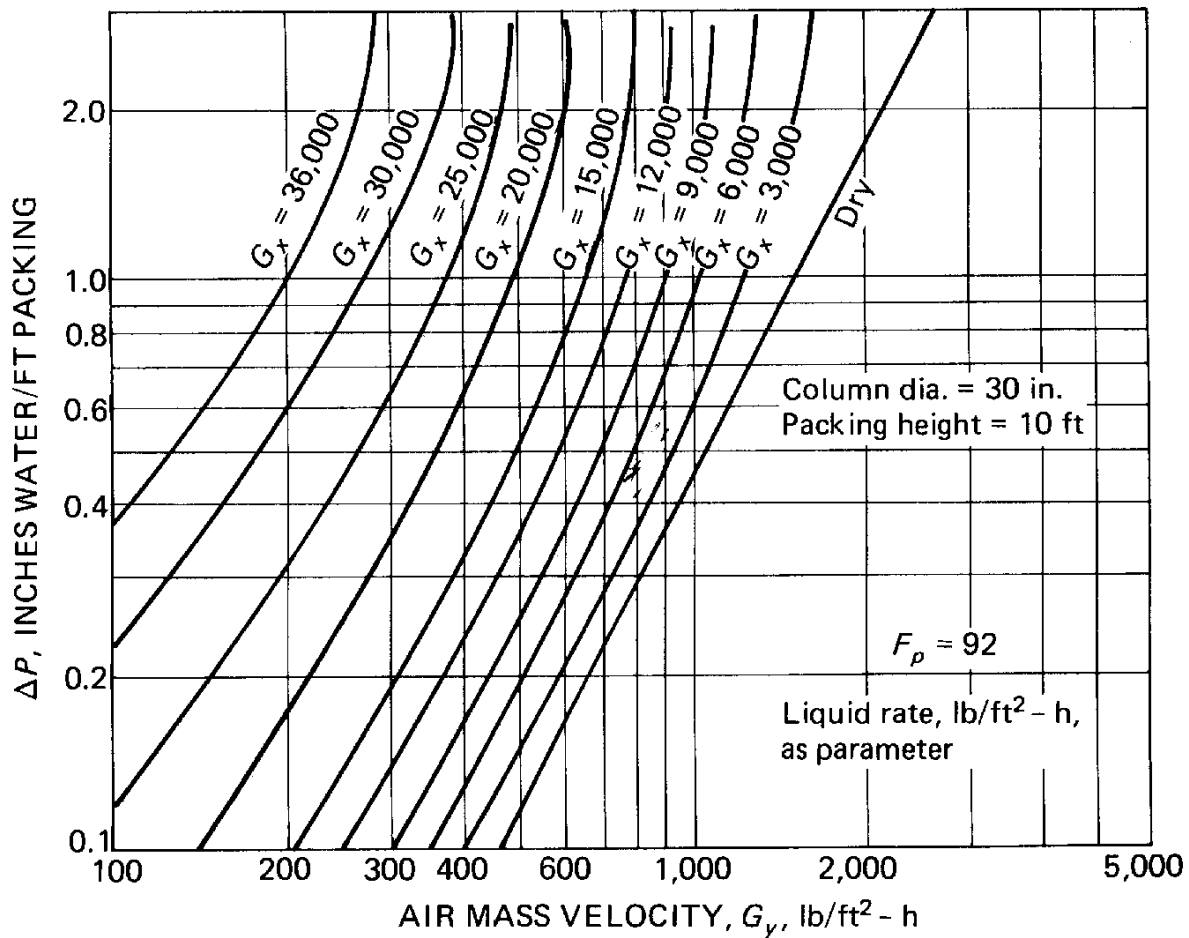
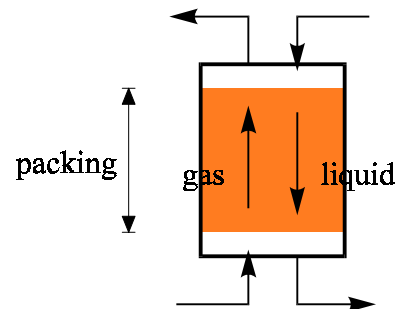


Fig. 8. Pressure drop across a packed bed of 1-inch ceramic Intalox saddles as a function of air and water flowrates. Taken from Fig. 22-4 of MS&H5.

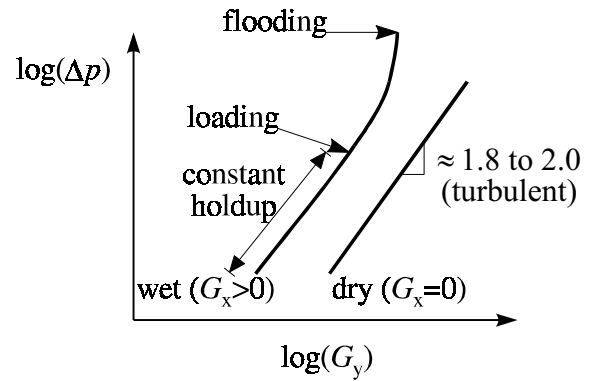
PRESSURE DROP IN PACK BEDS

Usually, flow in a packed-bed absorber is countercurrent. Gravity causes the liquid to flow down through the packing, whereas a small pressure drop drives the gas flow upward. This pressure drop plays an important role in packed beds. Without liquid present, the pressure-drop across dry packing increases approximately with the square of the gas flowrate (see Fig. 8).

$$G_y = \text{mass velocity of gas} = \frac{\text{lb / hr of gas}}{\text{cross - section of tower}} = \frac{M_y V}{S}$$

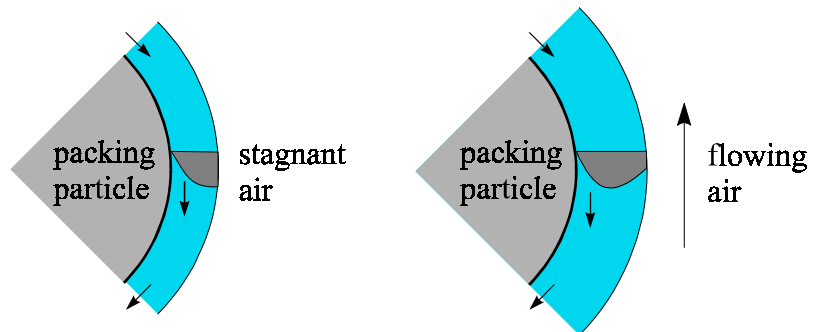


where M_y is the average molecular weight of the gas. Once liquid is flowing down the column as gas is flowing up, some of the space between the packing particles is taken up by liquid, leaving less space for the gas to flow. Forcing the same gas flow through a smaller opening will increase the frictional contribution to the pressure drop. Thus the curves for increasing liquid flow are above that for dry packing although the curves tend to be parallel.



Note that the curves with liquid flow curl up at high gas flow rates. This can be explained as follows:

The upward flow of the gas exerts a shear force on the liquid, retarding its downward motion. As the gas flowrate increases so does this shear force. When the shear force becomes comparable to gravity, the liquid flow might slow down and liquid begins to accumulate in the tower.



The amount of liquid residing or accumulating in the tower is called:

(liquid) holdup -- fraction of interstitial volume occupied by liquid

interstitial volume -- "empty" space between and inside packing particles; that volume occupied by liquid or gas.

loading -- an increase in liquid holdup caused by an increase in gas flowrate

For a given liquid flowrate, there is a maximum flowrate of gas which can be forced through the column. If you exceed this maximum the shear forces on the liquid are so high that they exceed the weight of the liquid. Then the net force on the liquid is upward and you blow the liquid back out the top of the column. This is called:

flooding -- liquid downflow is essentially stopped by high gas upflow

Since you can't get the liquid through the column, flooding is clearly a condition to be avoided. Generally, to get a high area of contact between liquid and gas, you want to operate well below the flooding velocity:

at flooding:

$$\Delta p_f/L \approx 2 \text{ to } 3 \text{ inch H}_2\text{O/ft of packing}$$

loading: $\Delta p_f/L \approx 0.5$ inch H₂O/ft

normal oper.: $\Delta p_f/L \approx 0.25$ to 0.5 inch H₂O/ft

Normal operating pressure drops are just below those for which loading begins.

Notice (from Fig. 8) that when we increase the liquid flowrate, flooding occurs at lower gas flows. If we increase the size of the packing particle, we can tolerate higher gas flows. While higher gas flows can be obtained with larger packing particles, the amount of interfacial area is generally less (i.e. a is decreased). These effects are summarized by Fig. 9 at right.

Fig. 8 and Fig. 9 are for a particular packing (1" Intalox saddles) and for a particular temperature and pressure (20 °C and 1 atm). A more general correlation of pressure drop is provided by Fig. 10. The size and type of packing is accounted for in this correlation through the parameter

$$F_p = \text{packing factor}$$

Values of the packing factor for various

Symbol	Units
G_x, G_y	lb/ft ² -s
μ_x	cP
ρ_x, ρ_y	lb/ft ³
g_c	32.2 lb _f -ft/lb _m -s ²

types of packing are given in Fig. 11. The y-coordinate of this graph in Fig. 10 is not dimensionless, so you need to use the units summarized in the table at right.

TOWER DIAMETER

Once the total molar liquid and gas flowrates (L and V) are known, we can choose the diameter of tower we need. The diameter of the tower is usually chosen such that the pressure drop is some prescribed value below flooding:

choose D_T such that: $-\frac{dp}{dz} = \frac{\Delta p}{Z_T} \approx 0.25$ to 0.5 inch H₂O/ft of packing

The pressure drop depends on the *mass velocities*:

$$\frac{\Delta p}{Z_T} = f(G_y, G_x)$$

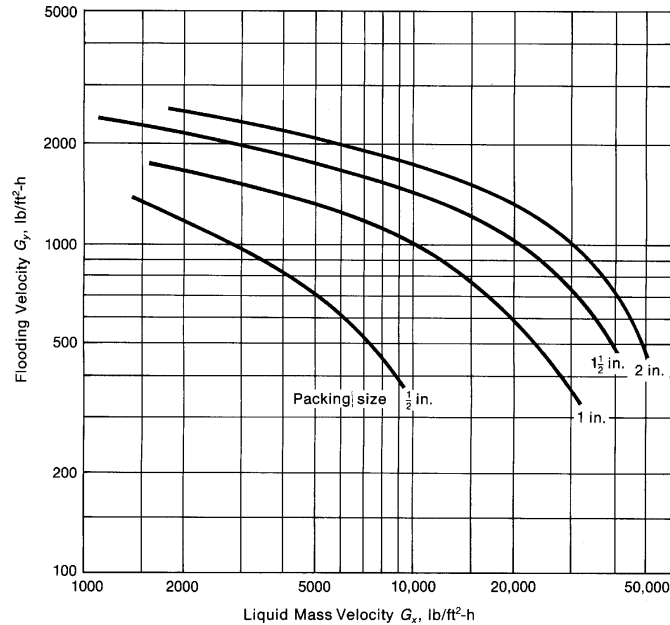


Fig. 9. Air flowrate at which flooding occurs for ceramic Intalox saddles at different water flowrates. Taken from Fig. 22.5 in MS&H5.

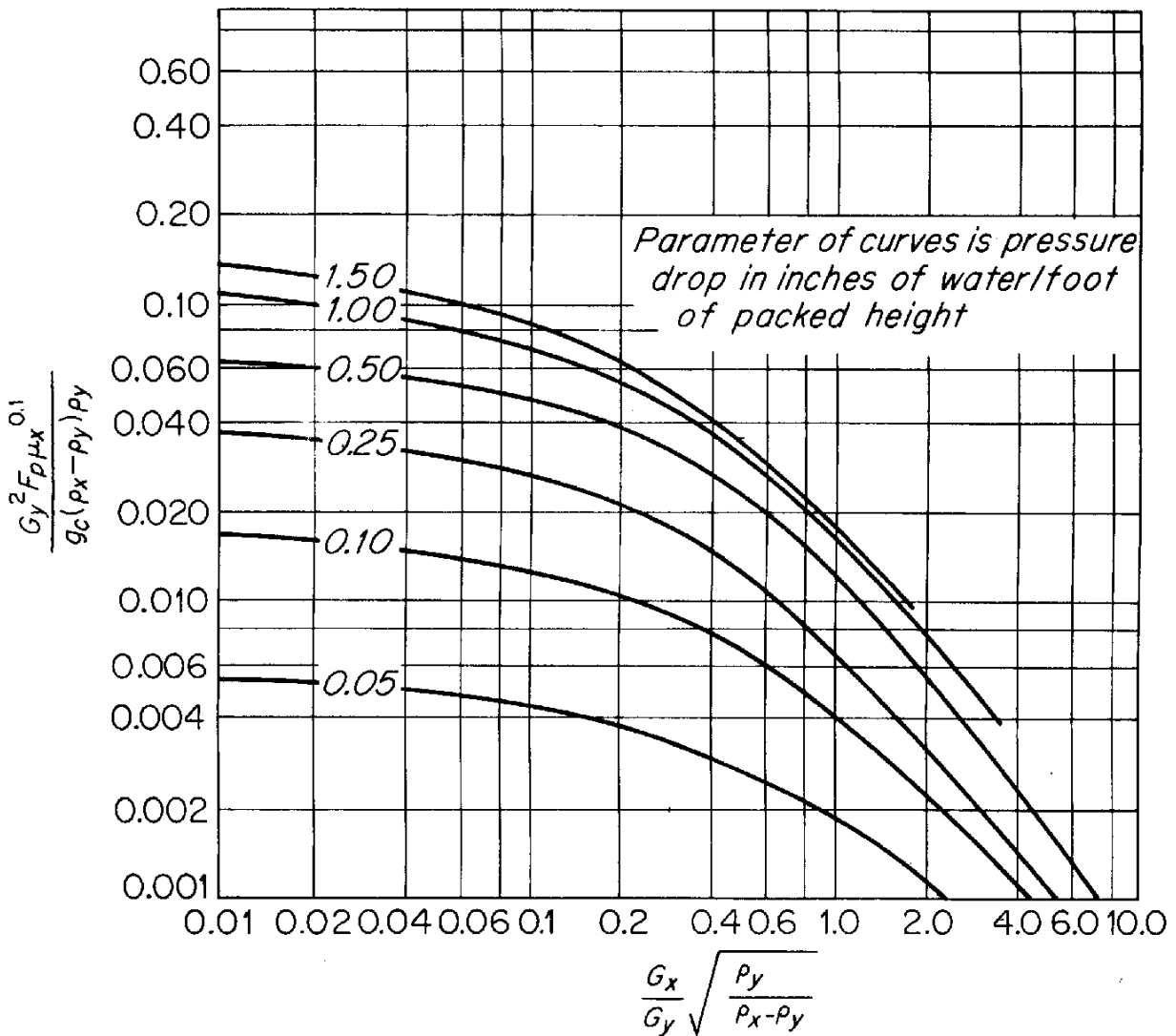


Fig. 10. General correlation of pressure drop across packed beds. Taken from Fig. 22.6 of MS&H5.

where

$$G_x \equiv \left\{ \frac{\text{mass flowrate of liquid}}{\text{cross-sectional area of column}} \right\} = \frac{M_x L}{S} = \frac{M_x L}{\pi D_T^2 / 4}$$

and where M_x is the average molecular weight of the liquid.

Similarly,

$$G_y = \frac{M_y V}{S}$$

Type	Material	Nominal size, in.	Bulk density, † lb/ft ³	Total area, † ft ² /ft ³	Porosity, ϵ	Packing factors ‡	
						F_p	f_p
Raschig rings	Ceramic	1/2	55	112	0.64	580	1.52§
		1	42	58	0.74	155	1.36§
		1 1/2	43	37	0.73	95	1.0
		2	41	28	0.74	65	0.92§
Pall rings	Metal	1	30	63	0.94	56	1.54
		1 1/2	24	39	0.95	40	1.36
		2	22	31	0.96	27	1.09
	Plastic	1	5.5	63	0.90	55	1.36
		1 1/2	4.8	39	0.91	40	1.18
		2	—	—	—	—	—
Berl saddles	Ceramic	1/2	54	142	0.62	240	1.58§
		1	45	76	0.68	110	1.36§
		1 1/2	40	46	0.71	65	1.07§
Intalox saddles	Ceramic	1/2	46	190	0.71	200	2.27
		1	42	78	0.73	92	1.54
		1 1/2	39	59	0.76	52	1.18
		2	38	36	0.76	40	1.0
Super Intalox saddles	Ceramic	3	36	28	0.79	22	0.64
		1	—	—	—	60	1.54
		2	—	—	—	30	1.0
IMTP®	Metal	1	—	—	0.97	41	1.74
		1 1/2	—	—	0.98	24	1.37
		2	—	—	0.98	18	1.19
Hy-Pak	Metal	1	19	54	0.96	45	1.54
		1 1/2	—	—	—	29	1.36
		2	14	29	0.97	26	1.09

† Bulk density and total area are given per unit volume of column.

‡ Factor F_p is a pressure-drop factor and f_p a relative mass-transfer coefficient.

§ Based on NH₃-H₂O data; other factors based on CO₂-NaOH data.

Fig. 11. Characteristics of common packings. Taken from Table 22-1 of MS&H5.

So to get a certain pressure drop for a certain set of flowrates, we must choose a particular value for the tower diameter. Although it looks like you have to guess the diameter D_T in order to calculate G_x and G_y , to get Δp , a trial-and-error can be avoided by noting that the abscissa (x -coordinate) does not depend on the diameter:

$$\frac{G_x}{G_y} = \frac{M_x L / S}{M_y V / S} = \frac{M_x L}{M_y V}$$

Note that the unknown cross-sectional area S conveniently cancels out. What remains is known. So the procedure is as follows:

Given: L, V

Find: D_T

Solution:

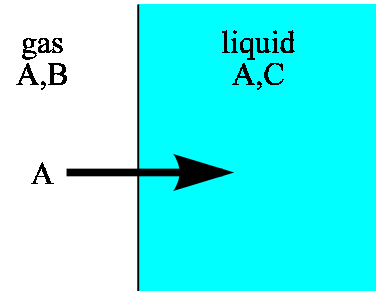
1. calculate the abscissa
2. locate the point on the curve of Fig. 22-6 which has the desired Δp and this value of the abscissa
3. read the corresponding ordinate of this point from Fig. 22-6
4. calculate G_y which gives this value for the ordinate
5. calculate the desired tower diameter from

$$\frac{\pi D_T^2}{4} = S = \frac{M_y V}{G_y}$$

Chapter 15. Membrane Separation

In distillation, gas absorption, and extraction we have two immiscible phases which we bring into intimate contact.

Operation	Phases contacted
distillation	liquid and its vapor
gas absorption	liquid and another gas
solid extraction	solid and a liquid
liquid extraction	two immiscible liquids

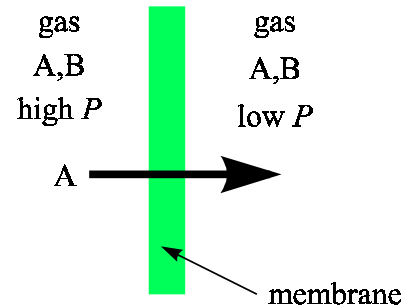


Another unit operation for mass-transfer is the *membrane separator*. Here the two phases are not immiscible — usually they are both gases or both are aqueous solutions. They are not intimately contacted; rather, a membrane is placed between them.

This membrane serves two functions:

1. keeps phases from mixing

This is also the primary function of the pipe wall in HXer; however, the membrane has a second, even more important, function. Whereas the pipe wall plays a passive role in heat transfer, the membrane plays an active role:



2. controls selectivity

Because of differences in molecular size or solubility of the gas in the membrane material, different species diffuse through the membrane at different rates. This difference is the basis of separation.

EXAMPLES

With the proper choice of membrane material, a membrane separator can achieve significant separations in a single stage. Indeed, as we shall see, it usually turns out that multistage operations with membranes are not economical (compared to cryogenic distillation). Thus most industrial applications of membranes do not require very high purity products.

Gases

- **separation of $^{238}\text{UF}_6$ from $^{235}\text{UF}_6$.** This was a very important part of the atom bomb project in World War II.

- **separation of O₂ from N₂ in air.** A number of industrial processes require a chemically inert gas (like nitrogen). Membranes can produce 95-99% nitrogen from air (79% nitrogen, 21% oxygen) in a single stage. Sometimes its the oxygen-rich stream that useful: 40-50% oxygen can be obtained from air, which is useful for medical patients having respiratory conditions.
- **recover H₂ from purge streams** in ammonia, methanol, and hydrogenation plants.
- **separation of He from CH₄** (natural gas). Because of its very small molecular size, half of the helium in a feed stream containing <1% He can be recovered in a single stage, resulting in a permeate stream contain 30 times greater concentration of He.

Liquids

- **dialysis** (or liquid permeation). Separation of urea and other small molecules from protein and cells in whole blood is accomplished in artificial kidneys. Recovery of caustic (NaOH) from hemicellulose produced in the manufacture of rayon.
- **electrodialysis.** Brackish water (containing less salt than sea water) can be made potable by applying electric field across membrane.
- **reverse osmosis.** Brackish water can also be made potable by applying pressure to force water through a membrane which is impermeable to ions.

In the 1950's, President Eisenhower was convinced that drinking water was the key to world peace in many parts of the world. Eisenhower's successor as President was John Kennedy. In a famous speech, President Kennedy expressed his intention to "land a man on the moon and make the deserts bloom." The second part of this quote has been obscured by the first part. Nonetheless, Kennedy did follow through by creating the Office of Saline Water, which provided financial support for much of the early research on membranes.

EQUIPMENT

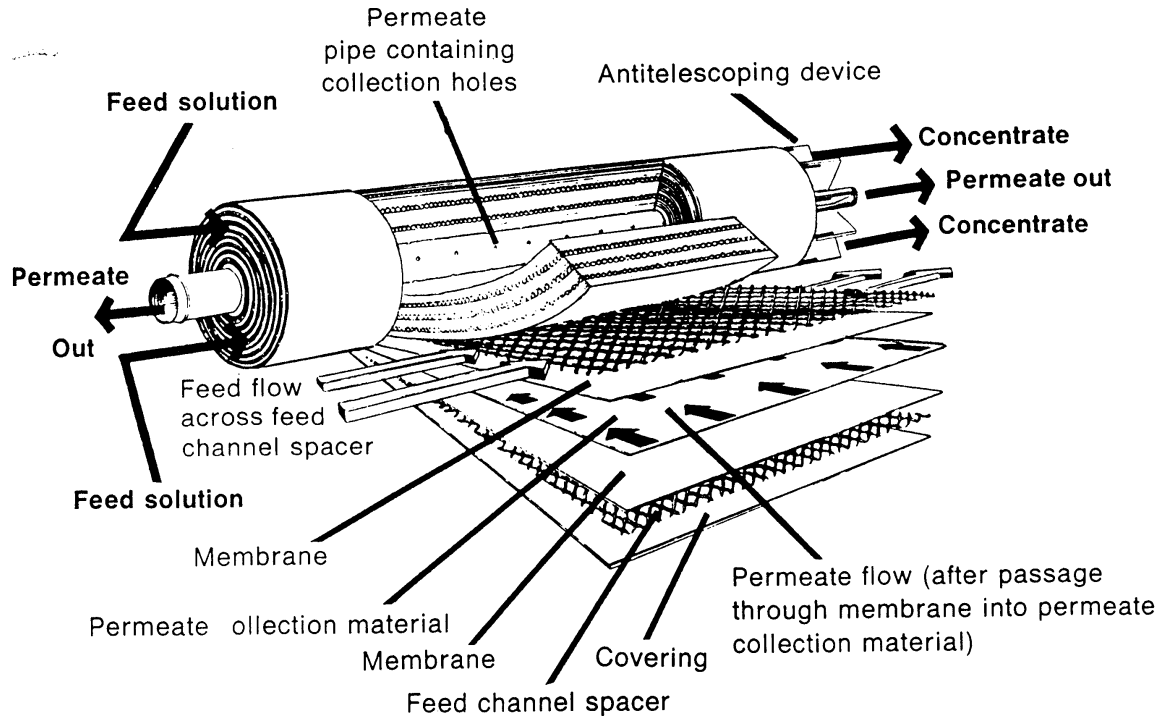


Fig. 12. A spiral-wound membrane

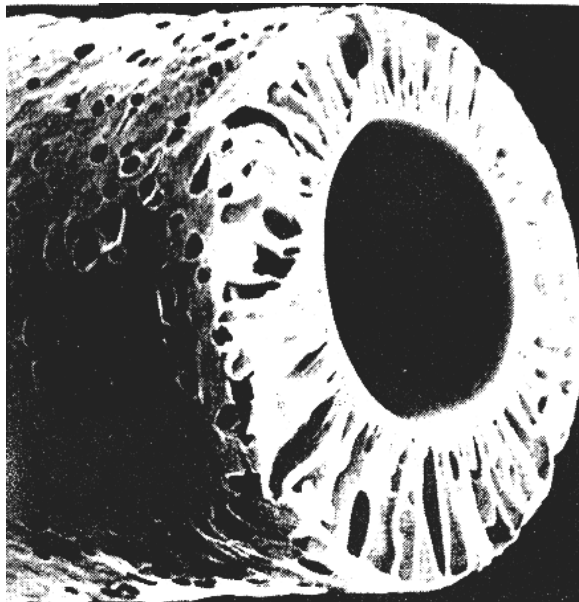


Fig. 13. Magnification of a hollow-fiber member. Outer diameter between 50-200 microns.

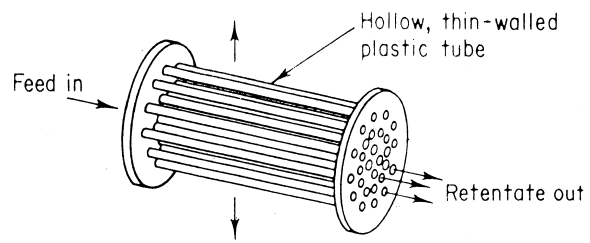


Fig. 14. A bundle of hollow fibers resembles a shell-and-tube heat

exchanger.

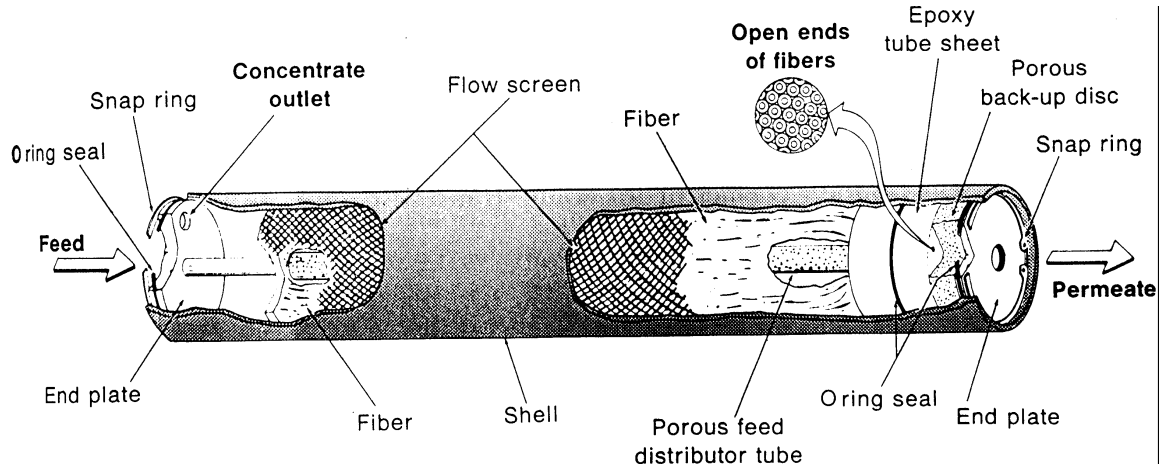


Fig. 15. A commercial cartridge containing hollow fiber membranes. This is a Permasep™ cartridge made by DuPont.

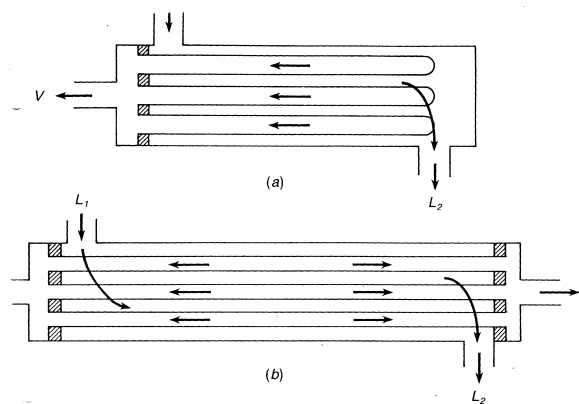


Fig. 16. Flow patterns inside bundle (side views). (a) shows hollow fibers with left ends sealed and right ends open to exit manifold. (b) shows hollow fibers with both ends open to exit manifolds.

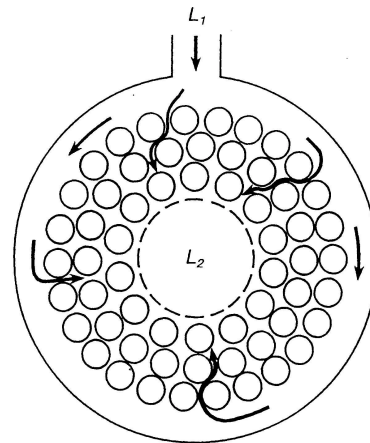


Fig. 17. Flow patterns inside bundle (end view).

SEPARATION OF GASES

Porous Membranes

Perhaps the simplest basis for separation of two gases is molecular size. Gases of different molecular weights have different diffusion coefficients and will diffuse at different rates through the membrane. For membranes having pores whose diameter is comparable or smaller than the mean-free path of gas molecules, the diffusion coefficient is inversely proportional to the square-root of molecular weight:

for Knudsen diffusion:

$$D_A = 9700r \sqrt{\frac{T}{M_A}} \quad (146)$$

where

r = pore radius (cm)

T = absolute temperature (K)

M_A = molecular weight of diffusing gas A

D_A = diffusion coefficient (cm²/s)

Notice that larger molecules (i.e. larger M_A) have smaller diffusion coefficients.

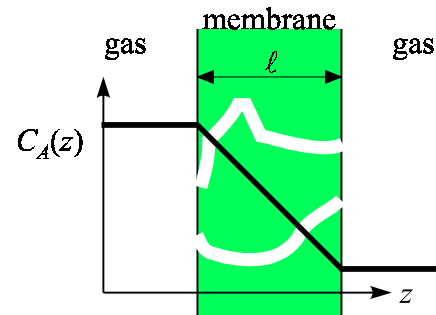
For membranes having fine pores through which the gas can diffuse, the fluxes of two gases, A and B , through a porous membrane are given by

$$J_{Az} = D_{Ae} \frac{C_A(0) - C_A(\ell)}{\tau \ell} \quad (147)$$

$$J_{Bz} = D_{Be} \frac{C_B(0) - C_B(\ell)}{\tau \ell}$$

where l is the thickness of the membrane and τ (which is greater than unity) is a dimensionless factor called the **tortuosity** which accounts for the fact that the pore length is generally larger than the thickness of the membrane.

Even if there are equal driving forces for the two components to diffuse across the membrane, they will have unequal concentrations on the downstream side because of their different diffusion coefficient. This is the basis for separation in a porous membrane.

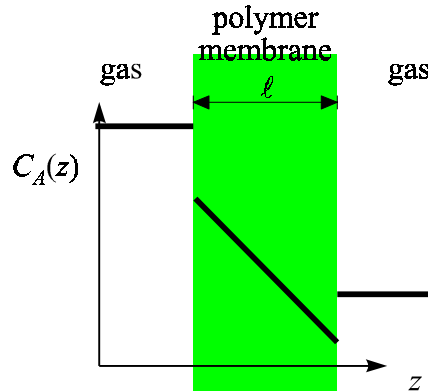


The best known example of gas separation by a porous membrane is separation of $^{238}\text{UF}_6$ from $^{235}\text{UF}_6$. Most gases have much smaller molecules than these and polymer membranes are used instead of porous membranes

Nonporous Polymer Membranes

Many polymer membranes do not have pores. Instead, the gas must first dissolve in the polymer. Then the dissolved gas diffuses through the membrane, which can be thought of as a liquid-like film. As a result, the concentration profile of the diffusing component A is not continuous (see figure at right).

Generally the mole fraction of the dissolved species is very small so that the equilibrium solubility of the gas in the solid can be described by **Henry's law**:



$$C_A = S_A P_A \quad \text{and} \quad C_B = S_B P_B \quad (148)$$

where

$$\begin{aligned} C_A &= \text{molar concentration of } A \text{ in membrane} \\ P_A &= \text{partial pressure of } A \text{ in gas} \\ S_A &= \text{solubility constant*} \end{aligned}$$

Again, at steady state the concentration profile inside the membrane will be linear and Fick's law yields:

$$J_{Az} = -D_A \frac{dC_A}{dz} = D_A \frac{C_A(0) - C_A(\ell)}{\ell} = D_A S_A \frac{P_A(0) - P_A(\ell)}{\ell} \quad (149)$$

For the purpose of comparison, the flux through a porous membrane [given by (147)] can also be written in terms of the partial pressures. For an ideal gas, the molar concentration C_A can be related to the partial pressure of the gas P_A by

$$\begin{aligned} P_A V &= n_A RT \\ C_A &= \frac{n_A}{V} = \frac{P_A}{RT} \end{aligned}$$

(147) becomes:

$$J_{Az} = \frac{D_A}{RT} \frac{P_A(0) - P_A(\ell)}{\ell} \quad \text{porous membrane}$$

(149):

$$J_{Az} = D_A S_A \frac{P_A(0) - P_A(\ell)}{\ell} \quad \text{polymer membrane}$$

* reciprocal of Henry's law constant

Although these two expressions have the same form, the coefficients are different. In particular, the solubility constant S_A varies much more between various gas solutes than does the diffusion coefficient D_A . This implies that polymer membranes tend to be much more selective in separation various gas species than porous membranes. Unfortunately, diffusion coefficients in solids and liquids are much smaller than for gases so this increase in selectivity is often traded off with lower permeation rates.

The product $D_A S_A$ is known as the

permeability coefficient: $q_A \equiv D_A S_A [=]$ Barrer

which has units of flux per unit pressure gradient. Since these complex units occur frequently in such problems, a new unit is defined, which is known as the **Barrer**:

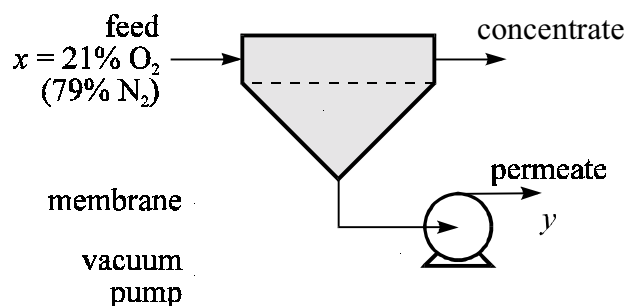
$$1 \text{ Barrer} \equiv 10^{-10} \frac{\underbrace{\text{cm}^3(\text{STP})}_{\text{rate}}}{\underbrace{\text{s}}_{\text{flux}}} \times \frac{1}{\underbrace{\text{cm}^2}_{1/\text{area}}} \times \frac{\text{cm}}{\underbrace{\text{cmHg}}_{dz/dP}} = 10^{-10} \frac{\text{cm}^3(\text{STP})}{\text{s} \cdot \text{cm} \cdot \text{cmHg}}$$

Often the thickness of the commercial membranes is not known. Then it is easier to measure the flux per unit *pressure*, rather than per unit *pressure gradient*. The flux per unit pressure drop is known as the

permeability: $Q_A \equiv \frac{D_A S_A}{\ell}$

EXAMPLE: PRODUCTION OF ENRICHED AIR

It turns out that most polymers are more permeable to O_2 than to N_2 . Let's see how this fact can be exploited to enrich the oxygen content of air. Consider the apparatus at right, which has one feed and two product streams. One of the product streams has been pulled through a polymer membrane with a vacuum pump.



The feed is normal atmospheric air which contains 21% oxygen and 79% nitrogen. We will denote these as components A and B . From our analysis of steady diffusion through the membrane, we know the fluxes of the two species must satisfy:

$$J_A = Q_A (P_{A1} - P_{A2}) = Q_A \left(xP_1 - y \underbrace{P_2}_{\ll P_1} \right) \approx xQ_A P_1 \quad (150)$$

$$J_B \approx (1-x)Q_B P_1$$

Because we are using a vacuum pump to pull the gas through the membrane, the pressure on the permeate side of the membrane will be much below atmospheric, thus:

for vacuum (on side “2”):
$$P_2 \ll P_1$$

This leads to the approximate expressions for the fluxes (above). Since the entire permeate stream must come through the membrane, the mole fraction of A in the permeate stream is determined by the relative amounts of the two species which come through. In time t the number of moles of species A which comes through a membrane of area A is $J_A A t$. Similarly, the number of moles of species B which comes through is $J_B A t$. The mole fraction of A is the number of moles of A divided by the total number of moles. The area and time cancel leaving

$$y = \frac{J_A A t}{J_A A t + J_B A t} = \frac{J_A}{J_A + J_B} \quad (151)$$

Substituting (150) into (151):

$$y = \frac{x Q_A P_1}{x Q_A P_1 + (1-x) Q_B P_1} = \frac{x Q_A}{x Q_A + (1-x) Q_B}$$

Notice that the total pressure cancels out. Finally, we divide the numerator and denominator by the permeability of gas B:

$$y = \frac{\alpha x}{\alpha x + (1-x)} = \frac{\alpha x}{(\alpha - 1)x + 1} \quad (152)$$

where
$$\alpha \equiv \frac{Q_A}{Q_B}$$

is called the **separation factor**. Its role is similar to relative volatility in distillation so we give it the same symbol. If we did not make the assumption of a vacuum on the downstream side, the analysis becomes a little more complicated, but still tractable. More generally, (150) becomes

$$\begin{aligned} J_A &= Q_A P_1 (x - R y) \\ J_B &= Q_B P_1 [(1-x) - R(1-y)] \end{aligned}$$

where
$$R \equiv \frac{P_2}{P_1}$$

and (152) becomes the root of the following quadratic equation:

$$R(\alpha - 1)y^2 - \{(\alpha - 1)(x + R) + 1\}y + \alpha x = 0 \quad (153)$$

Note that if $R = 0$, (153) reduces to (152). At right is a plot of y versus α for several different R 's. A couple of trends are apparent. First,

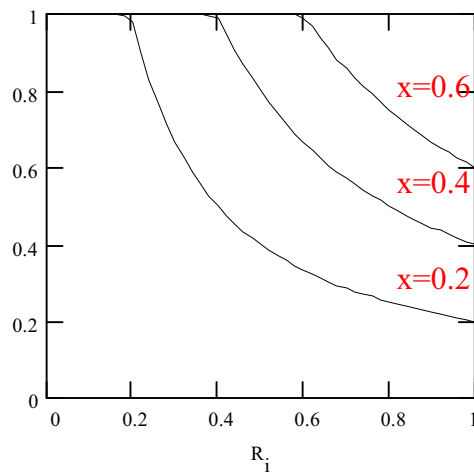
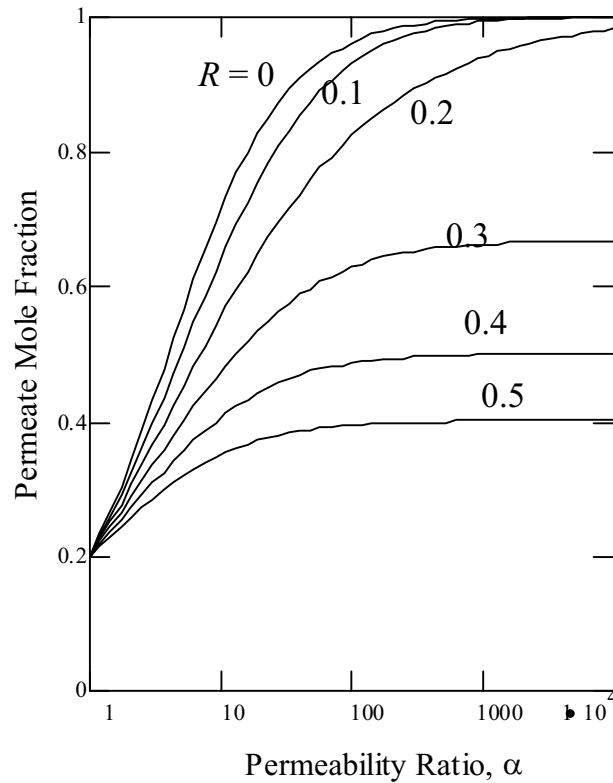
$$y \rightarrow x \text{ as } \alpha \rightarrow 1$$

$\alpha=1$ means there is no difference in permeability of the membrane to oxygen or nitrogen: then the permeate has the same concentration as the feed.

Second, note that the permeate tends to pure oxygen if the permeability ratio is high enough:

for $R < x$: $y \rightarrow 1$ as $\alpha \rightarrow \infty$

A closer look reveals that pure oxygen is only obtained if the pressure ratio is small enough. In particular, the ratio must be smaller than the feed molefraction.



The plot at left shows how $\lim_{\alpha \rightarrow \infty} (y)$ depends on the pressure ratio R . when $R < x$, then $y=1$. When $R=1$ (i.e. no driving force for flow through membrane), the permeate has the same concentration as the feed.

$R=1$ and $\alpha=\infty$: $y = x$

This behavior can be rationalized as follows: the partial pressure of oxygen in the permeate can never exceed that of the feed:

$$\underbrace{yP_2}_{P_{O_2 \text{ in permeate}}} \leq \underbrace{xP_1}_{P_{O_2 \text{ in feed}}} \tag{154}$$

Permeate concentration y in the limit as $\alpha \rightarrow \infty$ as a function of pressure ratio R .

but $P_2 = RP_1$ (155)

(155) into (154): $y \leq \frac{x}{R}$

If this inequality is not met, we would have diffusion uphill. The upper bound in oxygen partial pressure is reached when $\alpha \rightarrow \infty$:

$$\lim_{\alpha \rightarrow \infty} y = \min\left(1, \frac{x}{R}\right)$$

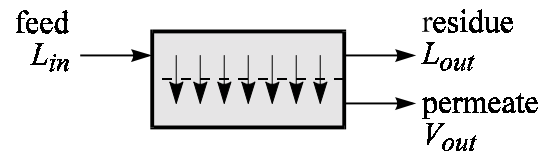
Stage Cut

Now let's look at a couple of complications. The fraction of the feed which permeates through the membrane is known as the **stage cut**:

$$\theta \equiv \frac{\text{total molar permeate rate}}{\text{total molar feed rate}} = \frac{V_{out}}{L_{in}}$$

When the stage cut is very small, then very little of the feed passes through the membrane

$$L_{out} \approx L_{in}$$

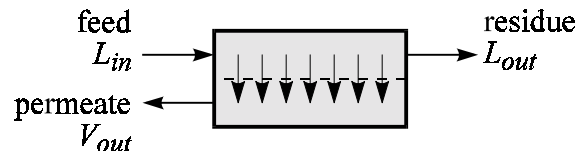


Co-current flow through separator

This also means the composition of the feed doesn't change much as a result of passing through the separator, so that

$$\text{stage cut} \ll 1: \quad x_{out} \approx x_{in}$$

Then every point on the membrane surface sees the same feed concentration x . This is what we have implicitly assumed in all of the above analysis. Under these conditions, it doesn't matter whether we operate the separator



Countercurrent flow through separator

cocurrently or countercurrently; we get the same y for both flow patterns. But this is not a very economical way to operate: very little of the feed is converted into product.

If the stage cut is not small, we will partially deplete the feed in the more permeable component: oxygen and x varies locally along the surface of the membrane.

for significant stage cut:

$$x_{out} < x_{in}$$

This complicates the analysis, because now there will be a continuous decrease in x and L as the feed gas moves along the surface of the membrane toward the residue.

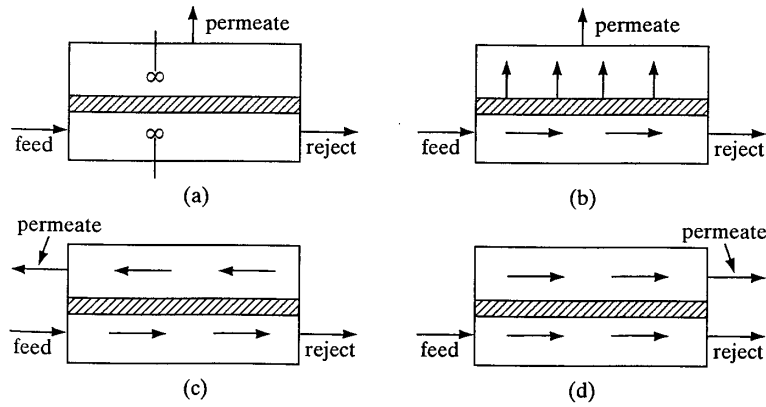


FIGURE 13.3-4. Ideal flow patterns in a membrane separator for gases: (a) complete mixing, (b) cross-flow, (c) countercurrent flow, (d) cocurrent flow.

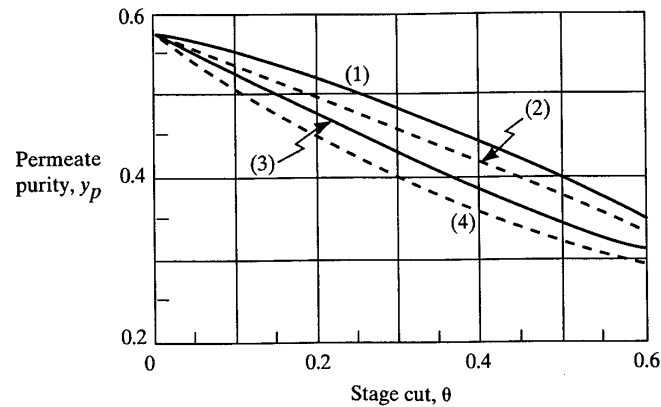


FIGURE 13.8-2. Effect of stage cut and flow pattern on permeate purity. Operating conditions for air are as follows: $x_f = 0.209$, $\alpha^* = 10$, $p_h/p_l = 380 \text{ cm Hg}/76 \text{ cm Hg} = 5$, $P'_A = 500 \times 10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm/s} \cdot \text{cm}^2 \cdot \text{cm Hg}$. (1) countercurrent flow, (2) cross-flow, (3) cocurrent flow, (4) complete mixing (W5). [Reprinted from W. P. Walawender and S. A. Stern, *Sep. Sci.*, 7, 553 (1972). By courtesy of Marcel Dekker, Inc.]

Fig. 13.8-2 shows the effect of stage cut on the permeate concentration for each of the 4 flow configurations illustrated in Fig. 13.3-4. These are calculated by carving the membrane into a large number of differential slices and then integrating the resulting equations.

Note that in general permeate concentration decreases with stage cut. This occurs because the local concentration on the feed side of the membrane is lower than at the inlet of the feed.

Chapter 16. Liquid-Liquid Extraction

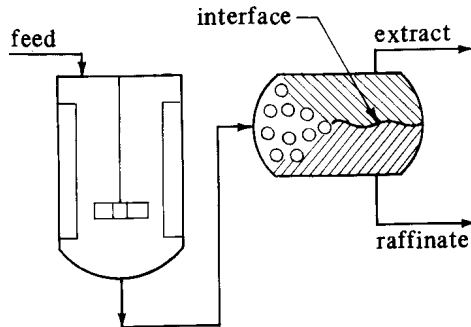
liquid-liquid extraction — separation of two components of a liquid (the “feed”) by contact with a second immiscible liquid (the “solvent”)

Extraction is used primarily when direct distillation is not economical (since the solvent usually has to be recovered by distillation). This might be the case with mixtures have very similar boiling points, or substances that cannot withstand the temperatures of distillation, even under vacuum. Examples include:

- extraction of penicillin from fermentation broth by contact with amyl or butyl acetate
- recovery of acetic acid from dilute aqueous solutions by contact with ethyl acetate (fingernail polish solvent) or ethyl ether
- separation of aromatics (rings) from aliphatics (straight chains) by contact with triethylene glycol
- separation of high-MW fatty acids from vegetable oil by contact with liquid propane

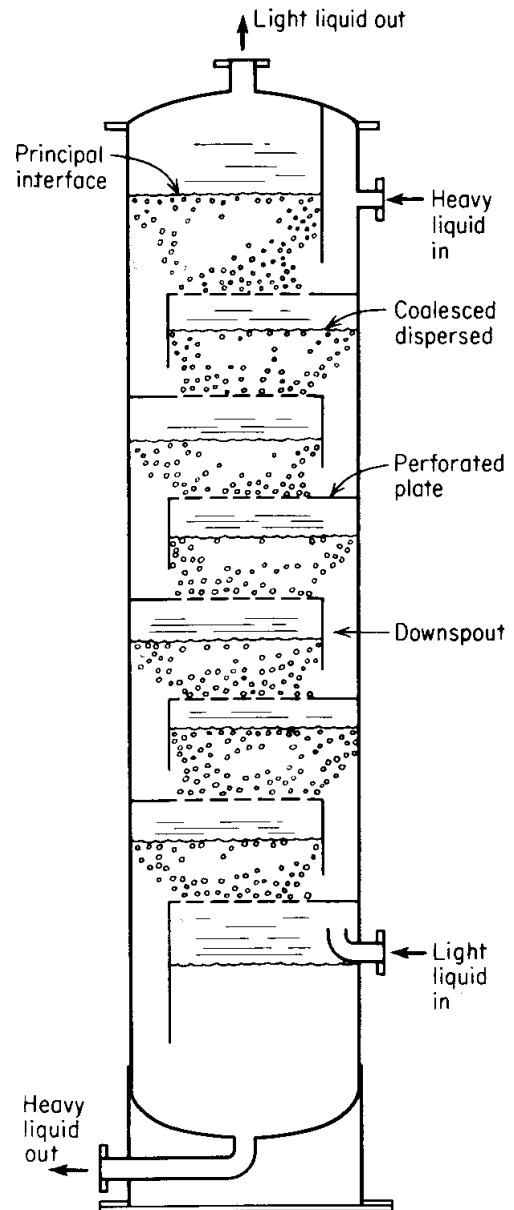
EQUIPMENT

Contacting of the two liquids might be performed in a countercurrent cascade of stages. Sometimes this can be accomplished in a sieve-tray tower like that used in distillation (see figure at right), where the difference in density drives the heavy fluid down while the lighter one floats upward.



More often a mechanical agitator is required to form the emulsion of the two immiscible liquids at each stage. One common design is the mixer-settler (shown above). The two liquid phases are fed to the tank where the mixer imparts mechanical energy and thus disperses one of the phases as fine droplets in the second phase (usually continuous). This state of mixtures is called an *emulsion*.

This emulsion is then transferred into a settler tank where the droplets begin to coalesce after the solute has redistributed across the liquid-liquid interface. Once the two phases have separated, the lighter one is drawn off the top (shown as “extract” in figure above) of the settler while the heavier one is drawn off the bottom (“raffinate”).



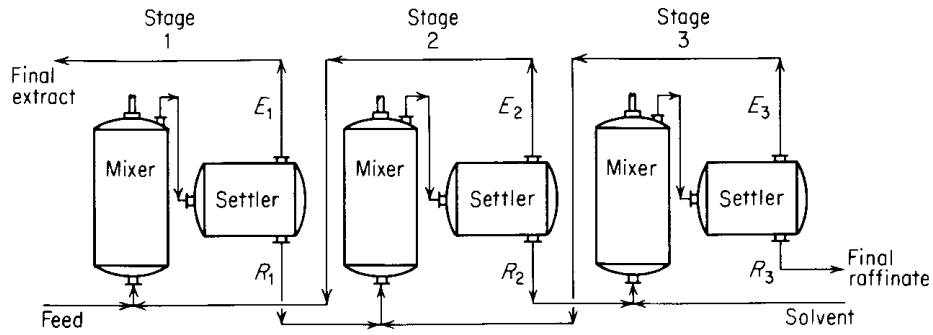


Fig. 10.5 Flow sheet of three-stage countercurrent mixer-settler extraction cascade.

Mixers-settlers can also be arranged as a countercurrent cascade of stages, as shown in the figure above.

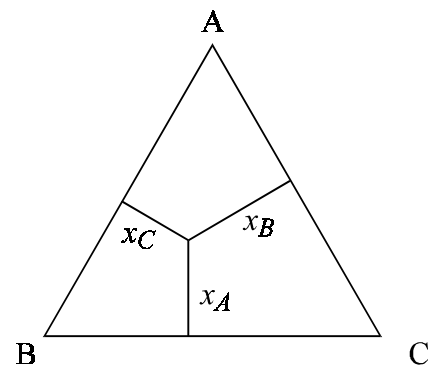
TRIANGLE DIAGRAMS

Many extraction systems involve three components which form two immiscible phases. For example, acetone and water are miscible in all proportions. When an organic solvent, methyl isobutyl ketone (MIK) is added to a water-rich acetone solution, two phases are formed: a water rich phase and an MIK-rich phase, both phases containing all three components. The composition of the two phases can be graphically represented by means of tie lines on a “triangle diagram.”

An equilateral triangle has the property that the sum of the lengths of the three normals drawn from any interior point to each side equals the height of the triangle, regardless of which interior point is chosen.

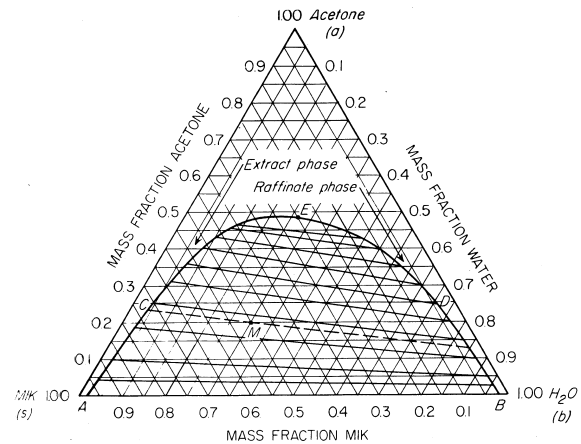
If we normalize the lengths of these three normals by the height, the normalized length can represent a mass fraction or a mole fraction of one of the three components. The geometry of the equilateral triangle assures that

$$x_A + x_B + x_C = 1$$



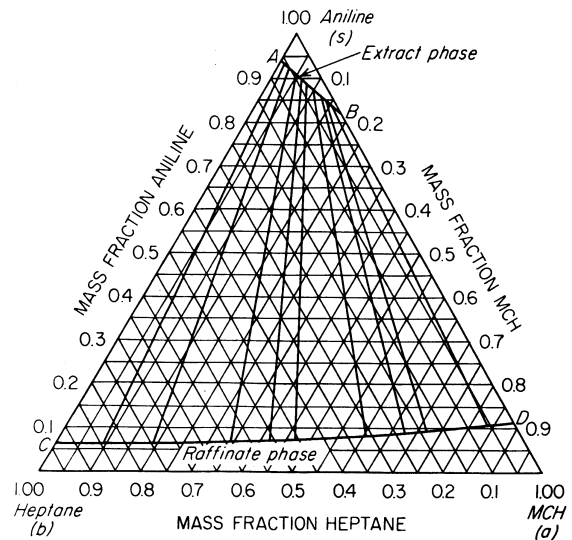
Thus each point inside the triangle represents the composition of a possible three-component mixture. A point at one of the three corners represents a pure component, while the normal distance between an interior point and the side opposite the corner for pure *A* represents the mole fraction or mass fraction of component *A* in the mixture.

The phase diagram for a mixture of acetone, methyl isobutyl ketone (MIK) and water at 25°C is shown at right. The shaded region (below the curve) represents compositions for which two immiscible liquid phases form, while the unshaded region (above the curve) are compositions for which only one phase forms. The nearly horizontal lines with the shaded region represent *tie lies* connecting the compositions of two liquid phases that co-exist at equilibrium.



In this system, acetone is completely miscible in both water and MIK, but MIK is only slightly soluble in water and water is only slightly soluble in MIK. This is an example of a **Type I** triangle diagram.

A very different looking triangle diagram results when one of the liquids is not completely miscible with either of other two. The diagram at right is for the system aniline-heptane-methylcyclohexane. This is an example of a **Type II** triangle diagram.



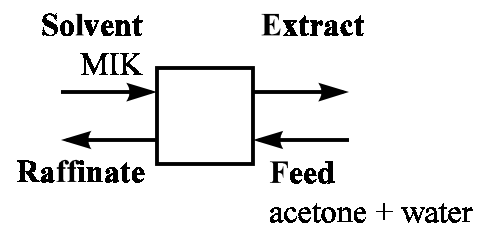
NOMENCLATURE

Notice in the Type I triangle diagram that as the fraction of acetone gets higher, the tie lines get shorter. Eventually, the tie line becomes infinitesimally short, such that the composition of the two immiscible phases become equal at the

plait point — point on the triangle diagram at which the composition of the two immiscible phases are equal.

Under normal operation we contact the “feed” stream with a “solvent” stream, producing two immiscible liquid phases which are separated to form two streams, which are called the “extract” and the “raffinate.”

extract — product stream which is richer in the solvent (the remains of the solvent stream after the solute has joined it)



raffinate — product stream which is leaner in the solvent (what remains of the feed after the solute has been extracted)

RECTANGULAR DIAGRAMS

While triangle diagrams are commonly used to present the phase diagram for three-component mixtures, the geometry of an equilateral triangle complicates construction. Three-component phase behavior can also be presented using a rectangular diagram, an example of which is shown at right for a ternary system of Type I.

As with an (equilateral) triangle, the point at each apex of this (right) triangle represents one of the three components in the pure state. Each of the three sides of the triangle represents mixtures in which one of the three components is completely absent. For example, the base of the right triangle at right represents mixtures of acetic acid and water which do not contain any ether.

The hypotenuse of the right triangle corresponds to

$$x_A + x_C = 1 \quad \text{or} \quad x_B = 0$$

where the subscripts denote components. Lines parallel to the hypotenuse correspond to

$$x_A + x_C = \text{const} < 1 \quad \text{or} \quad x_B > 0$$

if the line lies below the hypotenuse and

$$x_A + x_C = \text{const} > 1 \quad \text{or} \quad x_B < 0$$

if the line lies above the hypotenuse. Clearly, the latter situation is impossible so that points outside the right triangle are extraneous.

FLASH MIXING OF TWO LIQUIDS

Suppose we take two immiscible liquids (formed of the same three components: A, B and C) and mix them. What will be the composition of the mixture? Let

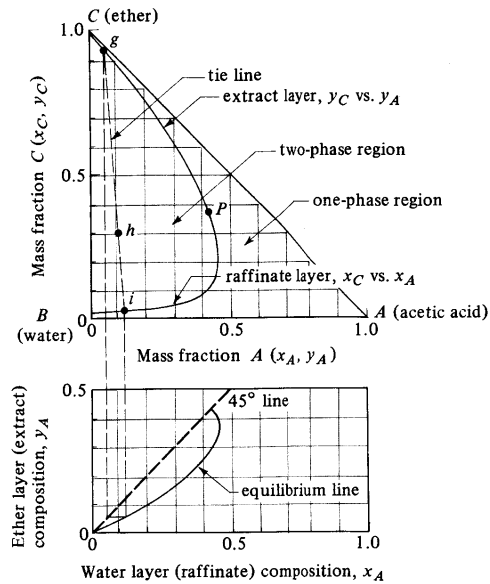
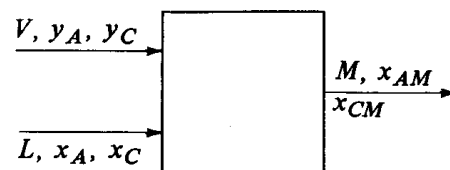


FIGURE 12.5-3. Acetic acid (A)-water (B)-isopropyl ether (C) liquid-liquid phase diagram at 293 K (20°C).



$L, V =$ total mass flowrate of the two liquid input streams

$M =$ total mass flowrate of the output stream (ignoring the phase distribution)

$x_A, x_C =$ mass fraction of components A,C in the stream having flowrate L

$y_A, y_C =$ mass fraction of components A,C in the stream having flowrate V

$x_{AM}, x_{CM} =$ mass fraction of components A,C in the stream having flowrate M

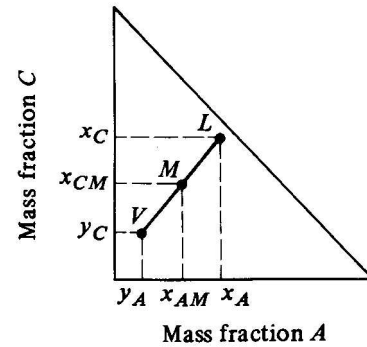
EXAMPLE #1: Given: L, V, x_A, x_C, y_A and y_C

Find: M, x_{AM} and x_{CM}

Solution: Here is a recipe for a graphical solution using a rectangular diagram (see figure at right).

Step 1: Locate points L and V on the rectangular diagram [coordinates are (x_A, x_C) and (y_A, y_C)]

Step 2: Locate point M on a straight line connecting L and V using the *inverse lever-arm rule*:



$$\frac{\overline{VM}}{\overline{LM}} = \frac{L}{V} \quad (156)$$

where \overline{LM} or \overline{VM} denote the length of the lines connecting points L and M or V and M, respectively.

Step 3: Read coordinates of point M as (x_{AM}, x_{CM}) .

Proof: A total mass balance is

$$L + V = M \quad (157)$$

and mass balances on components A and C yield:

$$Lx_A + Vy_A = Mx_{AM} \quad (158)$$

$$Lx_C + Vy_C = Mx_{CM} \quad (159)$$

Substituting (157) into (158): $Lx_A + Vy_A = (L+V)x_{AM}$

Collecting terms, we obtain $L(x_A - x_{AM}) = V(x_{AM} - y_A)$

or

$$\frac{L}{V} = \frac{y_A - x_{AM}}{x_{AM} - x_A} \quad (160)$$

Similarly combining (157) and (159), we obtain

$$\frac{L}{V} = \frac{y_C - x_{CM}}{x_{CM} - x_C} \quad (161)$$

Equating (160) and (161):

$$\frac{y_A - x_{AM}}{x_{AM} - x_A} = \frac{y_C - x_{CM}}{x_{CM} - x_C}$$

or

$$\underbrace{\frac{x_{CM} - y_C}{x_{AM} - y_A}}_{\text{slope of line } \overline{VM}} = \underbrace{\frac{x_C - x_{CM}}{x_A - x_{AM}}}_{\text{slope of line } \overline{LM}} \equiv \tan \theta$$

This shows that line segments \overline{LM} or \overline{VM} have the same slope and therefore point M must lie on line \overline{LV} . Moreover, (160) can be rewritten as

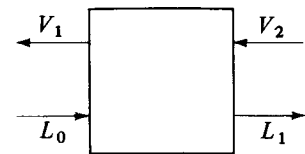
$$\frac{L}{V} = \frac{x_{AM} - y_A / \sin \theta}{x_A - x_{AM} / \sin \theta} = \frac{\overline{VM}}{\overline{LM}}$$

which proves (156).

SINGLE-STAGE EXTRACTOR

If point M in the previous example lies in the 1-phase region of the phase diagram, then we are done because we know the composition (x_{AM}, x_{CM}) of the single phase leaving the mixer. If the point M lies in the two-phase region and the two phases are allowed to reach equilibrium and separate in the settler, we will have (not one, but) two product streams.

Let's re-label the two input and two output streams as in the figure at right. In a typical extraction problem, stream L_0 is an aqueous solution containing a solute (component A) we are trying to extract by contact with an organic solvent (component C). So let's assume that the second feed stream (labelled V_2) is pure solvent. Let's try to determine the composition of the two product streams.



EXAMPLE #2: Given: $L_0, V_2, x_{A0}, x_{C0} = 0, y_{A2} = 0$ and $y_{C2} = 1$

Find: $L_1, V_1, x_{A1}, x_{C1}, y_{A1}$ and y_{C1}

Solution: Here is a recipe for a graphical solution using a rectangular diagram (see figure at right).

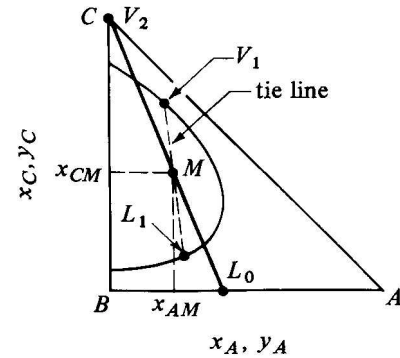
Step 1: Locate points L_0 and V_2 on the rectangular diagram
[coordinates are $(x_{A0}, x_{C0}=0)$ and $(y_{A2}=0, y_{C2}=1)$]

Step 2: Locate the mixing point M as in Example #1

Step 3: Find the tie line which passes through M

Step 4: The endpoints of this tie line represent L_1 and V_1
[coordinates are (x_{A1}, x_{C1}) and (y_{A1}, y_{C1})]

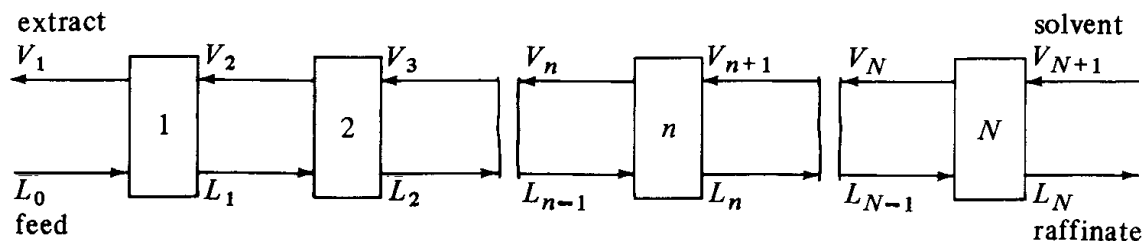
Step 5: The flowrates L_1 and V_1 can be determined using the reverse of the procedure for determining the mixing point M in Example #1



Essentially the mixing point gives the composition of a hypothetical single-phase mixture formed from the two feed streams. According to a mass balance, this is the same mixture which would be formed by mixing the two product streams. In other words, M is the mixing point for either L_0 and V_2 or L_1 and V_1 .

MULTI-STAGE EXTRACTOR

If we are satisfied with the amount of solute we have been able to extract from the solution in the single-stage extractor, then we are done. If we desire to extract more of the solute (i.e. we wish to achieve a smaller value of x_{A1}) then multiple stages might be used. Let's specify an arbitrarily small value for x_{AN} , the concentration of solute remaining after N stages.



EXAMPLE #3: Given: $L_0, V_{N+1}, x_{A0}, x_{C0} = 0, y_{AN+1} = 0, y_{CN+1} = 1$ and x_{AN}

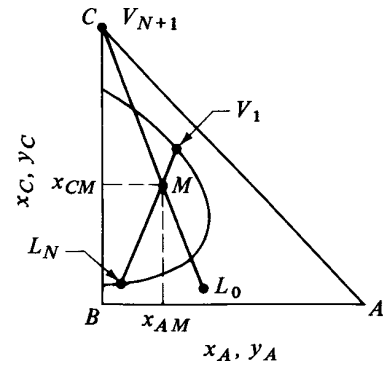
Find: L_N, V_1, x_{CN}, y_{A1} and y_{C1}

Solution:

Step 1: Locate points L_0 and V_{N+1}

Step 2: Locate their mixing point M . Read coordinates (x_{AM}, x_{CM}) and calculate $M = L_0 + V_{N+1}$.

This will also be the mixing point for the two product streams L_N and V_1 , although these streams are not coming from the same stage (i.e. they contain the same material as in the two feed streams). Assuming all the stages in the cascade are equilibrium stages, we also know that the points L_N and V_1 lie somewhere on the equilibrium curve, but not necessarily on opposite ends of the same tie line (since these streams are not coming from the same stage, they don't have to be in equilibrium with each other).



Step 3: Using the known value of x_{AN} , locate the point L_N on the lower portion of the equilibrium curve (i.e. on the raffinate portion of the curve). Read x_{CN} .

Step 4: Draw a straight line connecting L_N and M ; then extend this line until it crosses the equilibrium curve again.

Step 5: The intersection of this line with the equilibrium curve is point V_1 . Read the coordinates: (y_{A1}, y_{C1}) .

Step 6: Calculate the flowrates L_N and V_1 as the simultaneous solution of the following two equations:

$$\text{total mass balance:} \quad L_N + V_1 = M$$

$$\text{component C balance:} \quad L_N x_{CN} + V_1 y_{C1} = M x_{CM}$$

Everything in these equations is known except for the two unknowns: L_N and V_1 .

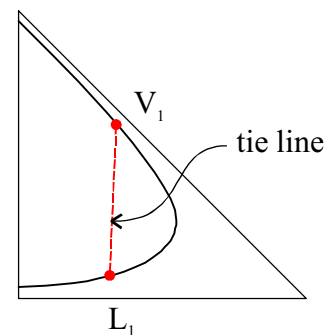
EXAMPLE #4: How many equilibrium stages are required to perform the separation described in Example #3? In other words, what is the value of N ?

Solution:

Step 1: Perform steps 1-6 in example #3 to locate point V_1 .

Step 2: Locate point L_1 at the other end of the tie line passing through V_1 .

After we remove extraneous lines and markings (for clarity), the rectangular diagram looks as shown at right.

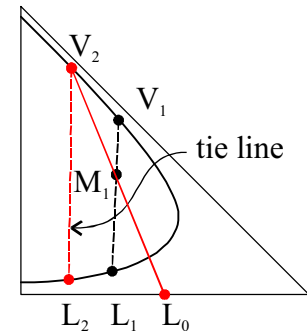


Step 3: Knowing the flowrates and compositions of the two output streams for stage #1, we can calculate the mixing point M_1 using the method of Example #1. This is also the mixing point for the two feed streams: L_0 and V_2 .

Step 4: Locate the point V_2 by connecting L_0 and M_1 with a straight line and extending it until it crosses the equilibrium curve.

Step 5: Locate L_2 at the other end of the tie line passing through V_2 .

Step 6: Repeat steps 3-5 (after incrementing all the subscripts by +1) until point L_N has an x -coordinate x_{AN} which equals or is smaller than that specified as x_{AN} for the entire cascade.



DIFFERENCE-POINT METHOD

Although the procedure in Example #4 works well (provided solvent flowrate V_{N+1} is above the minimum required), the coordinates of the mixing points M_1 , M_2 etc. have to be calculated manually. This tedious step can be avoided by observing that all the “operating lines” (i.e. L_0V_2 , L_1V_3 etc.) have a common point called the *difference point*.

Consider a total mass balance around some arbitrary stage in the cascade:

$$L_{n-1} + V_{n+1} = L_n + V_n$$

which can be rearranged to obtain

$$L_{n-1} - V_n = L_n - V_{n+1} \equiv \Delta \quad (162)$$

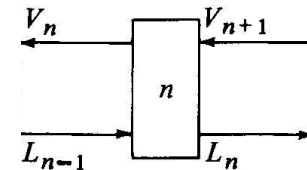
This difference between the flowrates of two “adjacent” streams in the cascade has exactly the same value for every stage in the cascade (i.e. $n = 1, 2 \dots N$). We denote this difference in flowrates by Δ . If instead of a total mass balance, we perform a mass balance on component A:

$$L_{n-1}x_{An-1} + V_{n+1}y_{An+1} = L_nx_{An} + V_ny_{An}$$

which can be rearranged to obtain

$$L_{n-1}x_{An-1} - V_ny_{An} = L_nx_{An} - V_{n+1}y_{An+1} \equiv \Delta x_{A\Delta} \quad (163)$$

Once again the difference the mass flowrates of component A in any two adjacent streams is exactly the same, regardless of which stage we pick. We denote this difference as $\Delta x_{A\Delta}$: the product of Δ and a fictitious mass fraction which we call $x_{A\Delta}$. The value of this fictitious mass fraction can be calculated by dividing (163) by (162) for $n=1$ (chosen because we know the flowrates and compositions of the two adjacent streams at the end of the cascade from Example #2):



$$x_{A\Delta} = \frac{L_0 x_{A0} - V_1 y_{A1}}{L_0 - V_1} \quad \text{and} \quad x_{C\Delta} = \frac{L_0 x_{C0} - V_1 y_{C1}}{L_0 - V_1} \quad (164)$$

An equation similar to this can be obtained for component C, which leads to the second equation above. The point $(x_{A\Delta}, x_{C\Delta})$ is called the ***difference point*** and is denoted by Δ . All the operating lines pass through this common point.

EXAMPLE #5: Repeat Example #4 using the difference-point method

Solution:

Step 1: Locate points L_0 and Δ . The coordinates of the latter are calculated from (164).

Step 2: Connect L_0 and Δ with a straight line.

Step 3: Locate V_1 as the point where this line crosses the (upper part of) the equilibrium curve

Step 4: Determine the tie line passing through V_1 . Locate L_1 as the other end of this tie line.

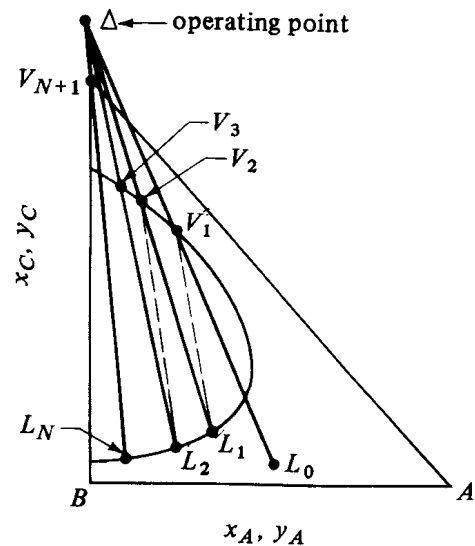
Step 5: Connect L_1 and Δ with a straight line.

Step 6: Locate V_2 as the point where this line crosses the (upper part of) the equilibrium curve

Step 7: Determine the tie line passing through V_2 . Locate L_2 as the other end of this tie line.

Step 8: Repeat steps 5-7 until the desired composition is obtained for L_N .

Proof (of difference point method):



Lecture #

Class Notes

**Unit Operations
of Chemical Engineering**

by

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