Separation Processes
ChE 4M3
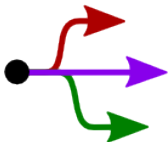
© Kevin Dunn, 2012

kevin.dunn@mcmaster.ca
http://learnche.mcmaster.ca/4M3

Overall revision number: 92 (October 2012)

Copyright, sharing, and attribution notice

We appreciate:

- ▶ if you let us know about **any errors** in the slides
- ▶ **any suggestions to improve the notes**

All of the above can be done by writing to
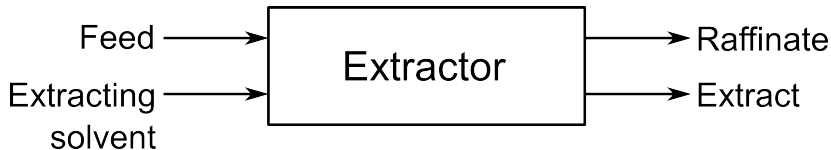
$$\texttt{kevin.dunn@mcmaster.ca}$$

If reporting errors/updates, please quote the current revision number: 92

Liquid-liquid extraction (LLE)

Definitions

- solute: species we aim to recover (A) from the feed
- feed or "feed solvent": one of the liquids in the system ("carrier")
- solvent: MSA (by convention: the "added" liquid)
- extract: solute mostly present in this layer $= y_A$
- raffinate: residual solute in this layer $= x_A$
- distribution: how the solute partitions itself $= D_A = \dfrac{y_A}{x_A} = \dfrac{y_E}{x_R}$

  - measure of affinity of solute
  - $D_A = \dfrac{\mu_R^0 - \mu_E^0}{RT} = \dfrac{\text{chemical potential difference}}{(R)(\text{temperature})}$

Where/why LLE is used

Where?

- Bioseparations
- Nuclear (uranium recovery)
- Mining: nickel/cobalt; copper/iron
- Perfumes, fragrances and essential oils
- Fine and specialty chemicals

Why?

- Temperature sensitive products
- High purity requirements
- High-boiling point species in low quantity
- Need to separate by species type (rather than relative volatility)
- Close-boiling points, but high solubility difference
- Azeotrope-forming mixtures

Extractor types
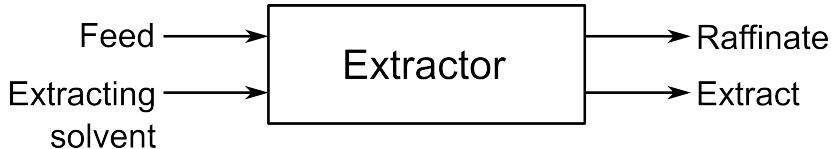
1. Mixing/contacting:
   - turbulent contact between liquid phases
   - small droplet dispersion in a continuous phase
     - which phase is dispersed?
   - mass-transfer between phases
   - limited by solute loading in solvent
2. Phase separation:
   - reverse of mixing step
   - drops coalesce
   - relies on density difference
3. Collection of phases leaving the unit

What are we aiming for?

Main aims
- High recovery of solute overall (low x_R and high y_E)
- Concentrated solute in extract (high y_E)

How to achieve this?
- Counter-current mixer-settlers in series
- High interfacial area during mixing
- Reduce mass-transfer resistance
- Promote mass transfer
  - molecular diffusion
  - eddy diffusion   ← orders of magnitude greater

Equipment for LLE

1. Mixer-settlers
   - mix: impellers
   - mix: nozzles
   - mix: feeds meet directly in the pump
   - mix: geared-teeth devices
   - main aim: good contact; avoid droplets smaller than 2 μm
   - settle: baffles, membranes
   - settle: ultrasound
   - settle: chemical treatment
   - settle: centrifuges
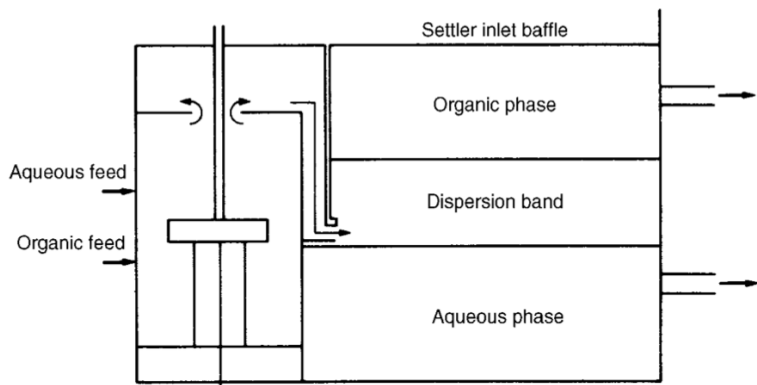2. Columns with:
   - (a) nothing or
   - (b) trays and/or
   - (c) packing and/or
   - (d) pulsating and/or
   - (e) agitation
3. Rotating devices

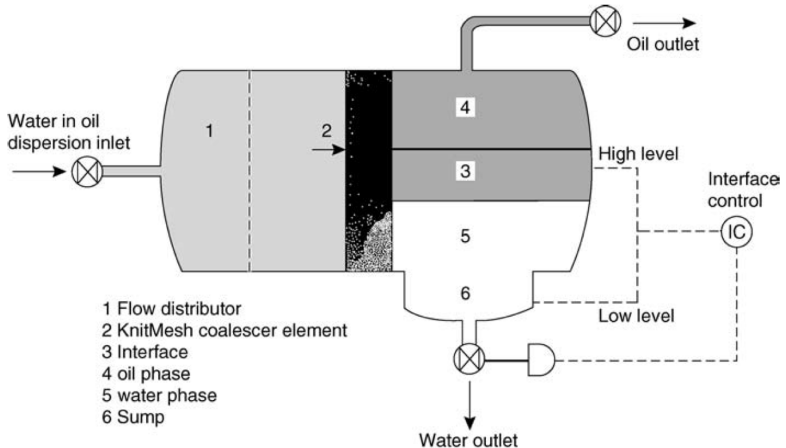Important point: LLE is an equilibrium-limited separation (as opposed to rate-limited separations seen up to now).

Mixer-settlers

Settler inlet baffle

Organic phase

Dispersion band

Aqueous phase

Aqueous feed

Organic feed

[Richardson and Harker, p 745] Common in mining industry: requirements ~40000 L/min flows

Mixer-settlers

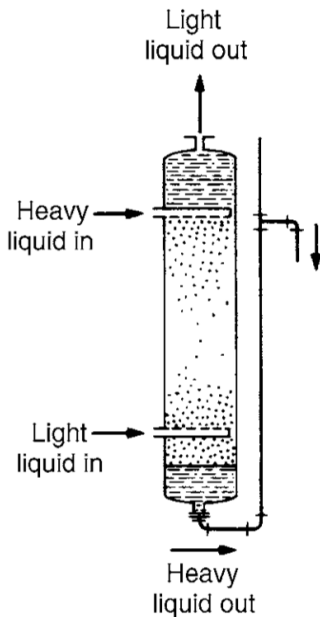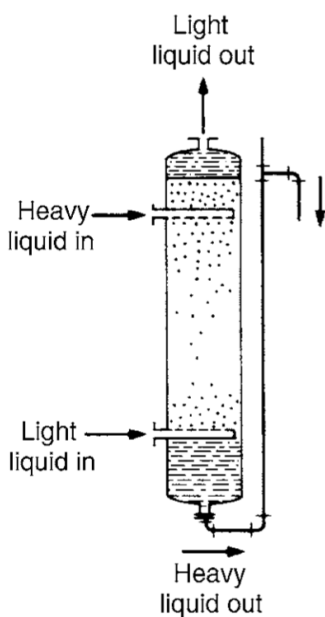KnitMesh coalescer: consistency of "steel wool"

Water in oil dispersion inlet

1 — Flow distributor
2 — KnitMesh coalescer element

Oil outlet

4 — oil phase
3 — Interface

High level

Interface control
(IC)

5 — water phase

6 — Sump

Low level

Water outlet

1 Flow distributor
2 KnitMesh coalescer element
3 Interface
4 oil phase
5 water phase
6 Sump

[Richardson and Harker, p 747]

Horizontal gravity settling vessel
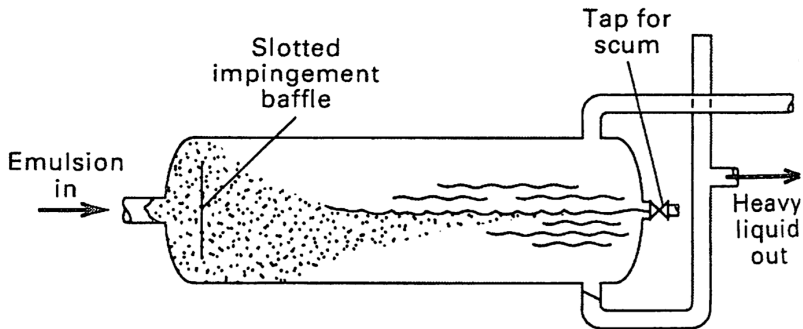
[Seader, 3ed, p302]

Spray columns: separation principle is gravity

Light liquid out

Heavy liquid in

Light liquid in

Heavy liquid out

Light liquid out

Heavy liquid in

Light liquid in

Heavy liquid out

[Richardson and Harker, p 751]
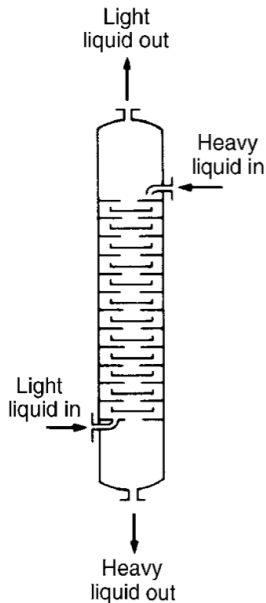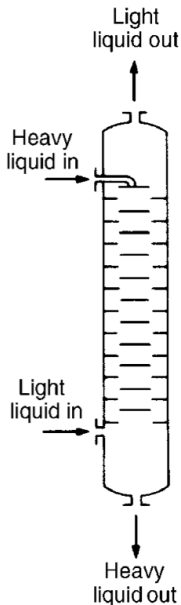
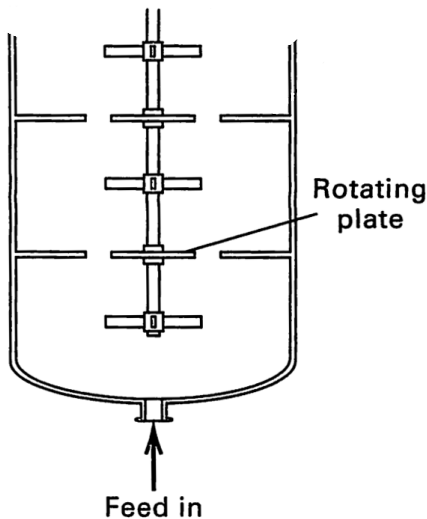# Tray columns

- coalescence on each tray
- tray holes: $\sim$ 3mm
- breaks gradient formation (axial dispersion)

Tray columns with mechanical agitation

Rotating plate

Feed in

- shearing to create dispersion
- can have alternating layers of packing (coalescence)
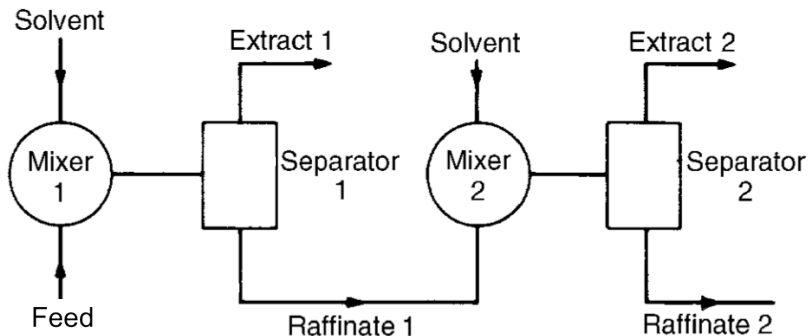- some column designs pulsate ⇑⇓

[Seader, 3ed, p302]

Rotating devices
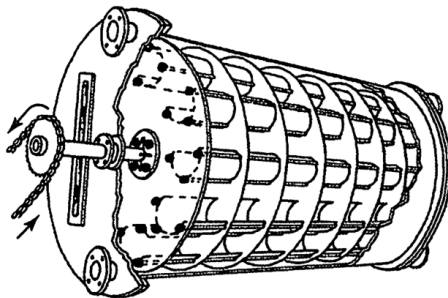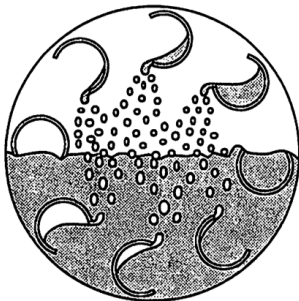
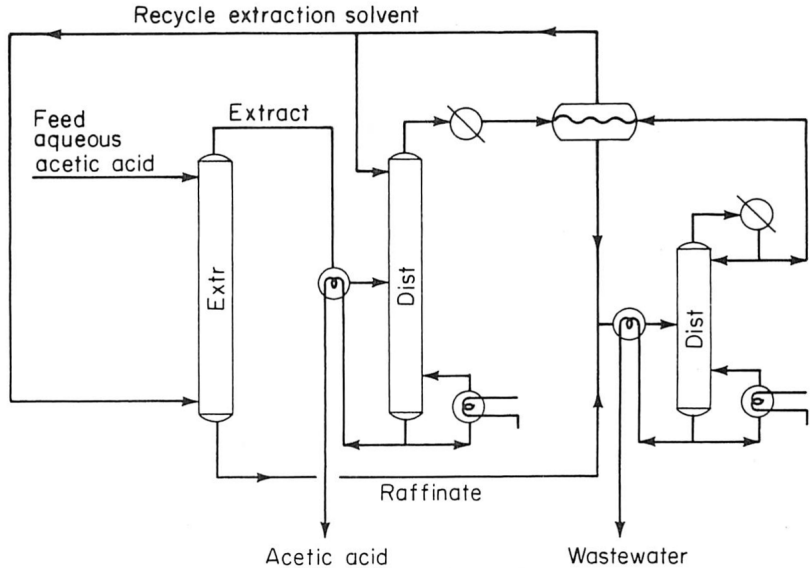- "white" = lighter liquid
- "grey" = heavier liquid

Used when foams and emulsions would easily form: i.e. gentle mass transfer.

Linking up units (more on this later)

[Richardson and Harker, p 723]

Integration with downstream units

Feed aqueous acetic acid · Recycle extraction solvent · Extract · Extr · Dist · Raffinate · Acetic acid · Wastewater · Dist

[Schweitzer, p 1-257]

Selecting a solvent

Schweitzer: "The **choice of solvent** for a LLE process can often have a more significant impact on the process economics than any other design decision that has to be made".

Which properties of a solvent influence our aims with LLE?

- High distribution coefficient (selectivity) for solute
- Low distribution coefficient for carrier
- Reasonable volatility difference with solute and carrier
- Reasonable surface tension: easy to disperse **and** coalesce
- High density difference: separates rapidly by gravity
- Stability to maximize its reuse
- Inert to materials of construction
- Low viscosity: maximizes mass transfer
- Safe: non-toxic, non-flammable
- Cheap, and easily available
- Compatible with carrier and solute: avoid contamination
- Doesn't foam, form emulsions, scum layers at interface

Calculating the distribution coefficient (in the lab only)

Mass balance:

$$Fx_F + Sy_S = Ey_E + Rx_R$$

$$D = \frac{y_E}{x_R}$$

If $F = S = E = R$ and $y_s = 0$, then only measure x_R:

$$D = \frac{x_F}{x_R} - 1$$

Feed

F

Extraction solvent   S → →E Extract

R

Raffinate

- ▸ Capital letters refer to mass amounts
- ▸ $y_\square$ ← refers to mass fractions in solvent layer
- ▸ $x_\square$ ← refers to mass fractions in carrier and extract layers

Once D is determined, we can obtain phase diagrams to understand how the process will operate.

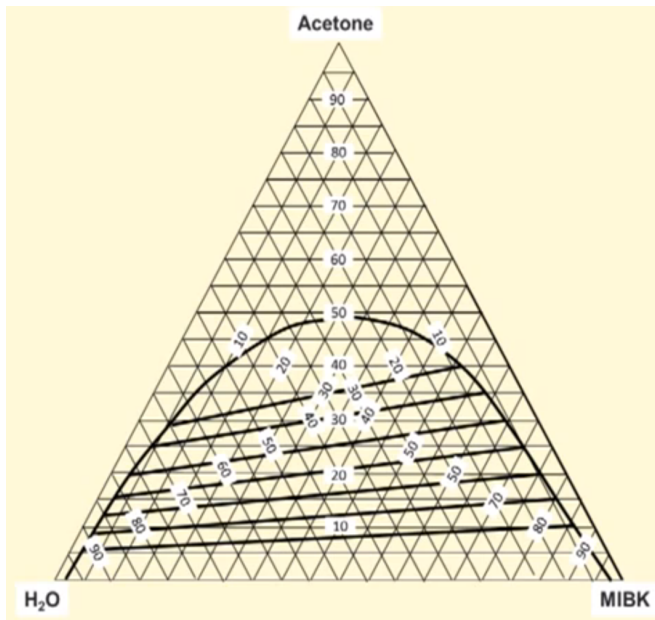Also: see Perry's for many values of D
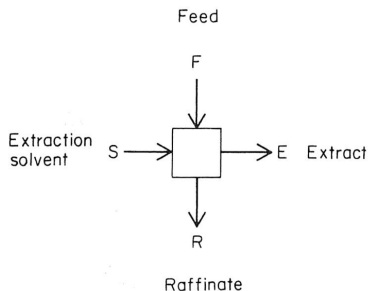
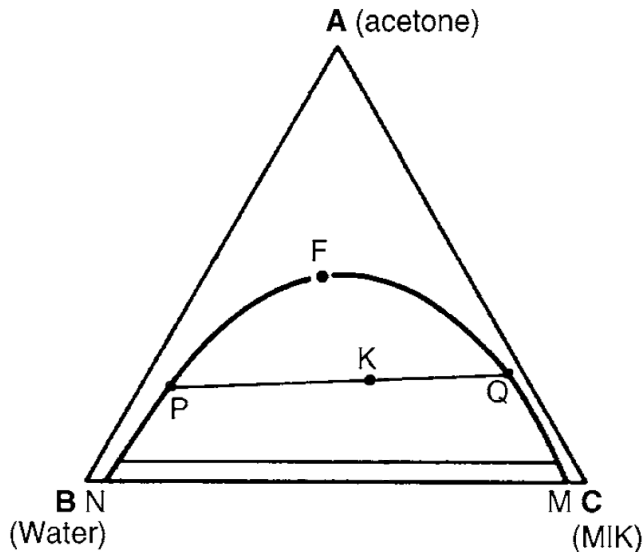# Triangular phase diagrams: from laboratory studies

Using a triangular phase diagrams
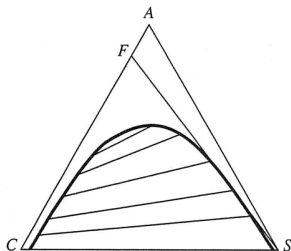
Lever rule

Mix P and Q

- mixture = K

- $\dfrac{PK}{KQ} = \dfrac{\text{amount } Q}{\text{amount } P}$

- The converse applies also: when separating a settled mixture
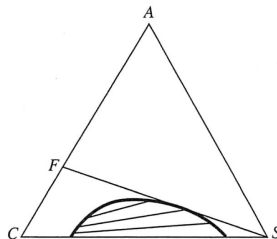
- Applies anywhere: even in the miscible region

Q1: Using the lever rule

Which is a more *flexible* system?

- ▶ S = pure solvent used
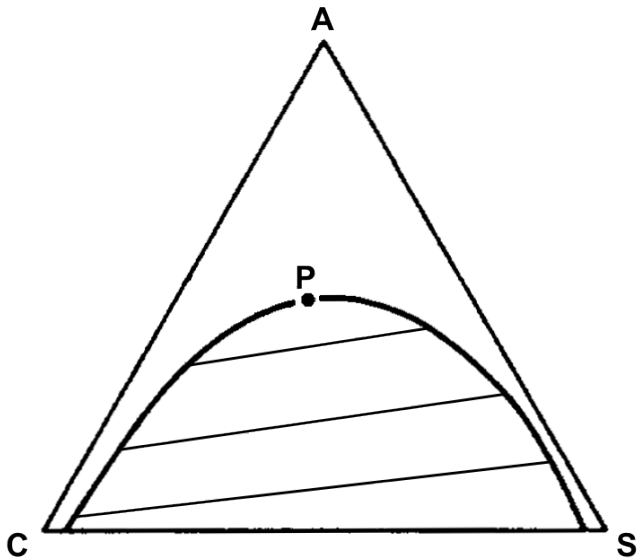- ▶ F = feed concentration point (more correctly it is x_F)
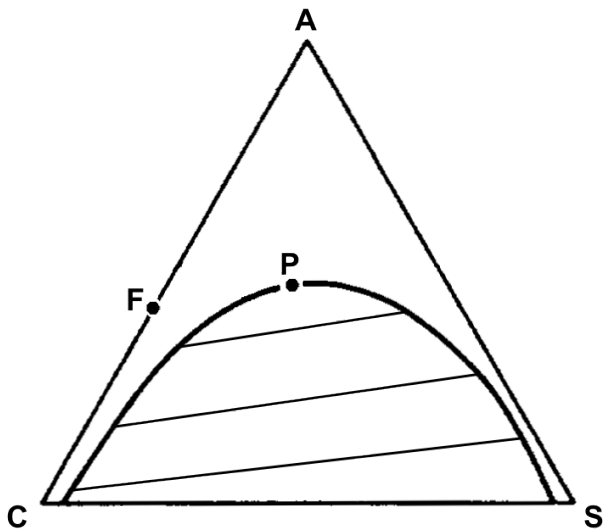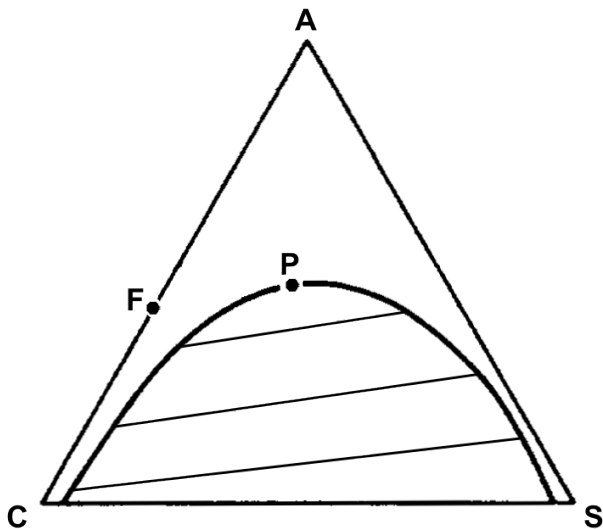

(a)   (b)

Answer:

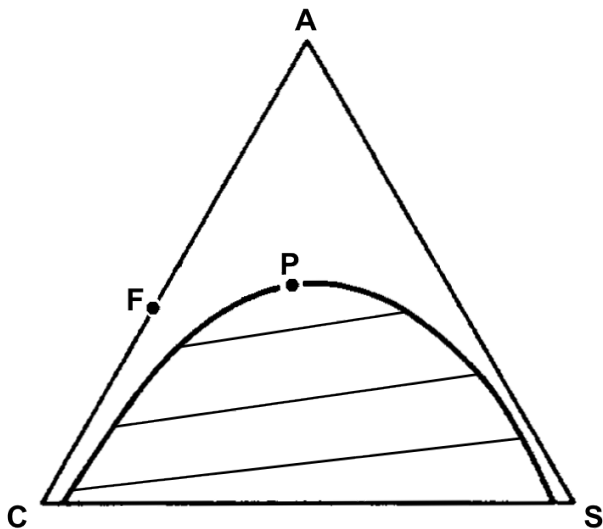Which is a more effective as a solvent: C or S ?

Mix a feed stream, F, containing C and A (i.e. x_f) with a pure solvent stream S (i.e. $y_S = 0$). Composition of the mixture?
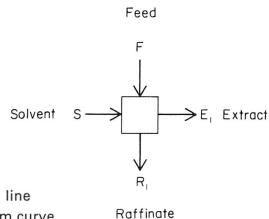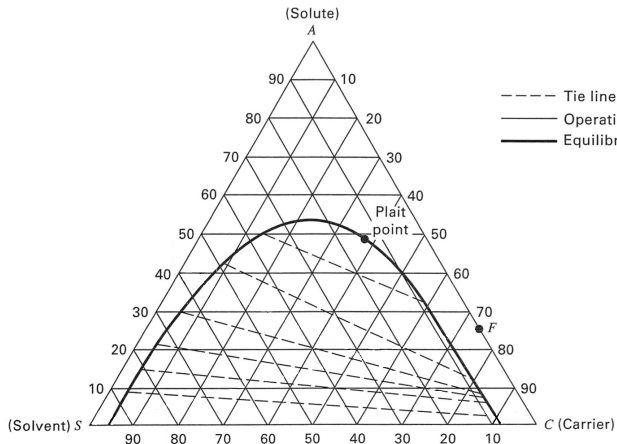
Q4: Going to equilibrium

Let that mixture M achieve equilibrium. What is the composition of the raffinate and extract?

Q5: Altering flows

Same system, but now lower solvent flow rate (to try save money!). What happens to (a) extract concentration and (b) solute recovery?
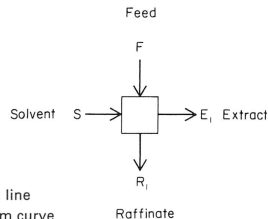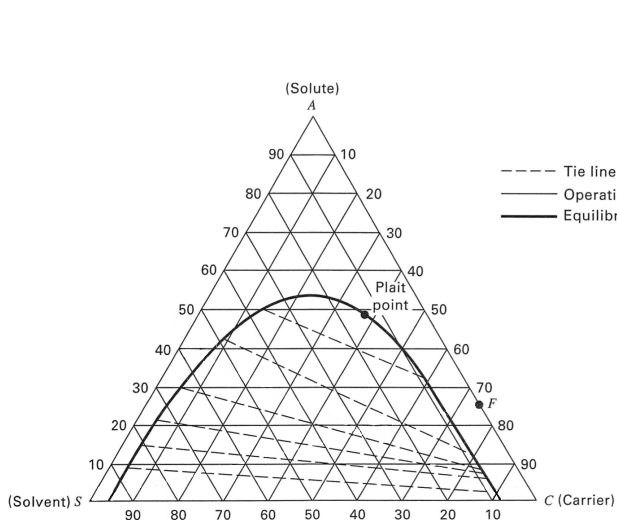
Q6: Composition of the mixture, M?

Feed	Solvent
$F = 250$ kg	$S = 100$ kg
$x_{F,A} = 0.24$	$x_{S,A} = 0.0$
$x_{F,C} = 0.76$	$x_{S,A} = 0.0$
$x_{F,S} = 0.00$	$x_{S,A} = 1.0$

Answer: $M = \qquad x_{M,A} = \qquad x_{M,C} = \qquad x_{M,S} =$

Q7: Composition of the 2 phases leaving in equilibrium?

Feed	Solvent
$F = 250$ kg	$S = 100$ kg
$x_{F,A} = 0.24$	$x_{S,A} = 0.0$
$x_{F,C} = 0.76$	$x_{S,A} = 0.0$
$x_{F,S} = 0.00$	$x_{S,A} = 1.0$

$R_1 = \qquad x_{R_1,A} = \qquad x_{R_1,C} = \qquad x_{R_1,S} =$

$E_1 = \qquad x_{E_1,A} = \qquad x_{E_1,C} = \qquad x_{E_1,S} =$

Link units in *series*
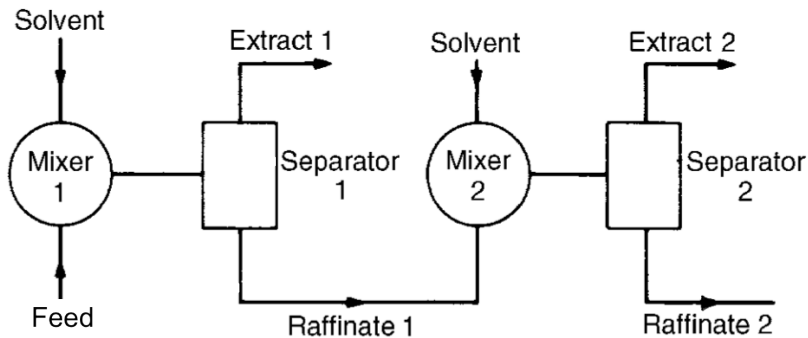
[Richardson and Harker, p 723]
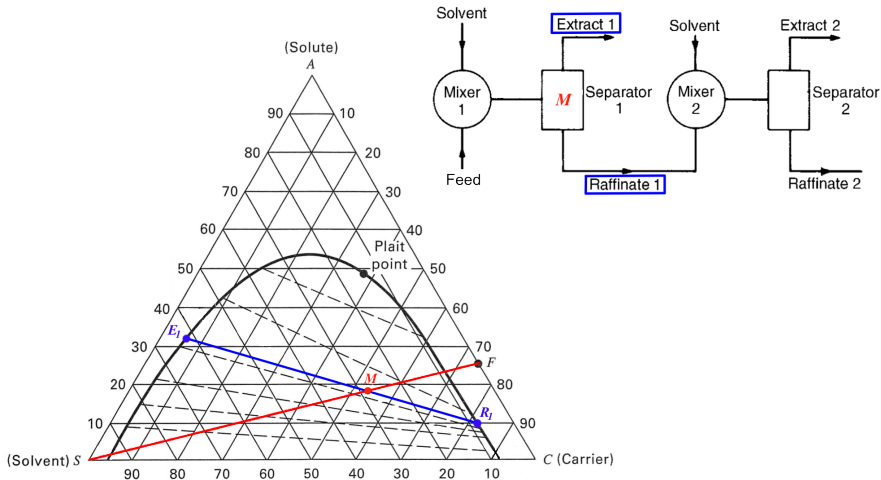
Question: how much solvent should we use in the second stage?

Some theory: Counter-current units
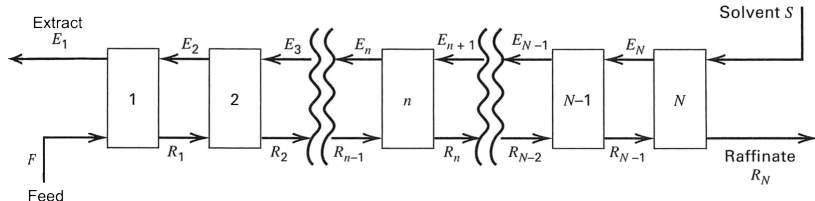
Just **consider 2 stages** for now. Mass balance at steady state:

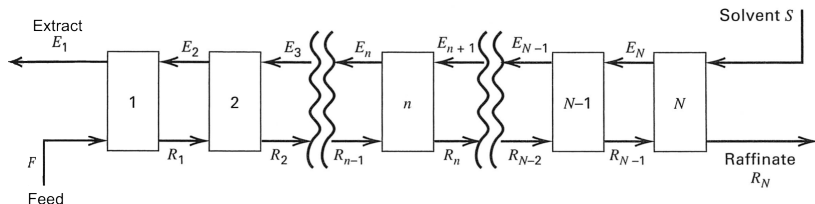$$F + E_2 = E_1 + R_1 \qquad\qquad E_2 + R_2 = S + R_1$$

Rearrange:

$$F - E_1 = R_1 - E_2 \qquad\qquad R_1 - E_2 = R_2 - S$$

$$F - E_1 = R_1 - E_2 = R_2 - S = P$$

So create P as a fictitious operating point

Counter-current graphical solution

Rearranging again:

$$F + P = E_1$$
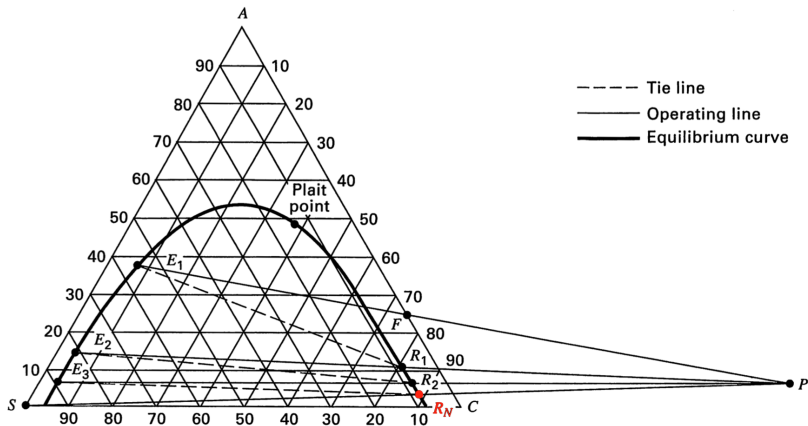$$R_1 + P = E_2$$
$$R_2 + P = S$$

Interpretation:

- P connects F and E_1
- P connects R_1 and E_2
- P connects R_{n-1} and E_n in general
- P connects R_N and S in general (or simply R_2 and S in the case of 2 units)

Counter-current graphical solution

- We know F and S; connect with a line and locate "mixture" M
- Either specify E_1 or R_N (we will always know one of them)
- Connect a straight line through M passing through the one specified
- Solve for the unspecified one

- Connect S through R_N and extrapolate to P
- Connect E_1 through F and extrapolate to P
- Locate P by intersection of 2 lines
- In general: connect E_n and R_n via equilibrium tie lines

References

- Schweitzer, "Handbook of Separation Techniques for Chemical Engineers", Chapter 1.9
- Seader, Henly and Roper, "Separation Process Principles", 3rd edition, chapter 8
- Richardson and Harker, "Chemical Engineering, Volume 2", 5th edition, chapter 13
- Geankoplis, "Transport Processes and Separation Process Principles", 4th edition, chapter 12.5 and 12.6
- Ghosh, "Principles of Bioseparation Engineering", chapter 7
- Uhlmann's Encyclopedia, "Liquid-Liquid Extraction", DOI:10.1002/14356007.b03_06.pub2