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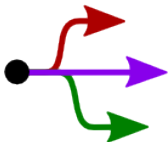
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kevin.dunn@mcmaster.ca
http://learnche.mcmaster.ca/4M3

Overall revision number: 107 (November 2012)

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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
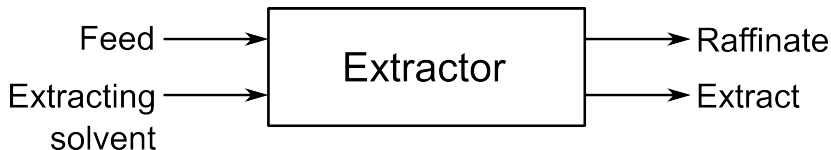
$$\texttt{kevin.dunn@mcmaster.ca}$$

If reporting errors/updates, please quote the current revision number: 107

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: solvent (not solute) mostly present in this layer.
  $y_{E,A}$ = concentration of A, the solute, in extract.
- ▶ raffinate: residual solute in this layer = $x_{R,A}$
- ▶ distribution: how the solute partitions itself = $D_A = \dfrac{y_{E,A}}{x_{R,A}}$

  - ▶ 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
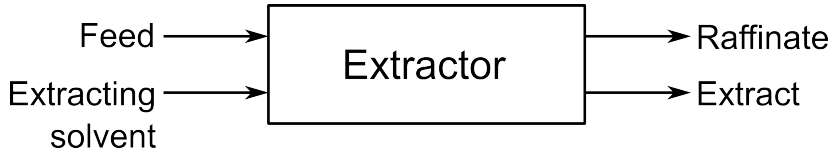
1. Mixing/contacting:
   - turbulent contact between liquid phases
   - small droplet dispersion in a continuous phase
      - which phase is dispersed?
   - mass-transfer between phases
   - limited by solute loading in solvent
2. Phase separation:
   - reverse of mixing step
   - drops coalesce
   - 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
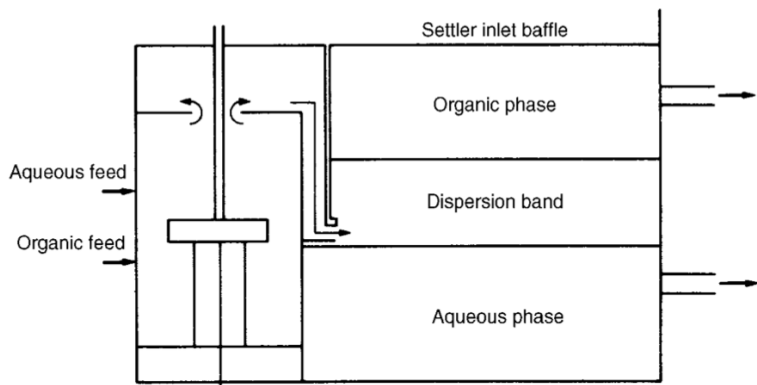2. Columns with:
   - (a) nothing or
   - (b) trays and/or
   - (c) packing and/or
   - (d) pulsating and/or
   - (e) agitation
3. Rotating devices

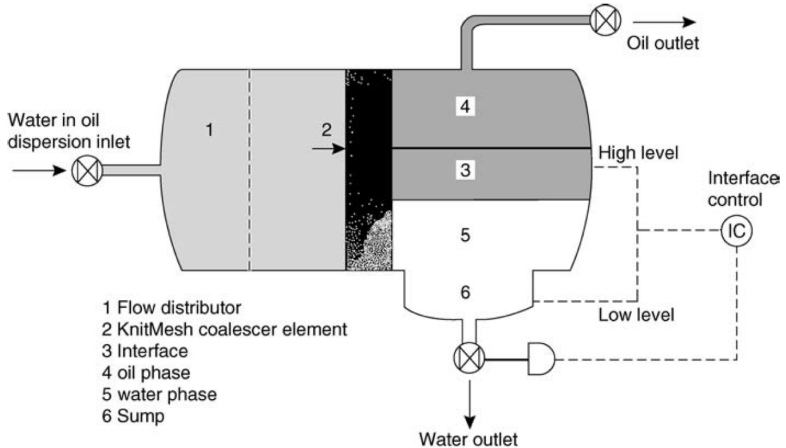Important point: LLE is an equilibrium-limited separation (as opposed to rate-limited separations seen up to now).

Mixer-settlers

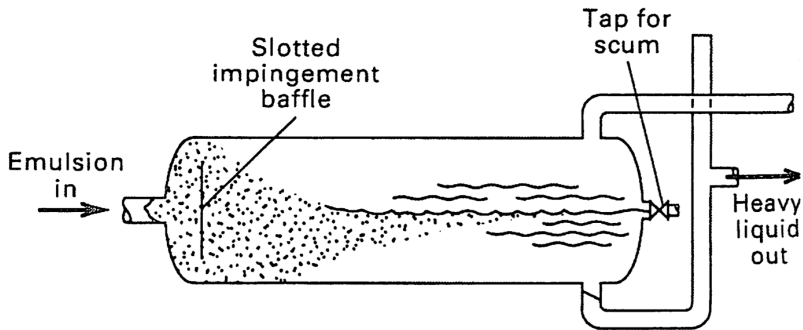[Richardson and Harker, p 745] Common in mining industry: requirements ~40000 L/min flows

Mixer-settlers

KnitMesh coalescer: consistency of "steel wool"

Water in oil dispersion inlet

Oil outlet

High level

Interface control

IC

Low level

Water outlet

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

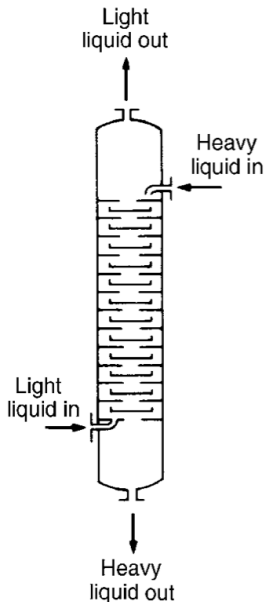[Richardson and Harker, p 747]

Horizontal gravity settling vessel
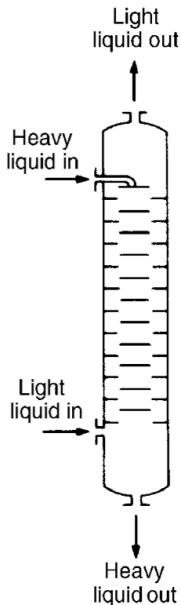

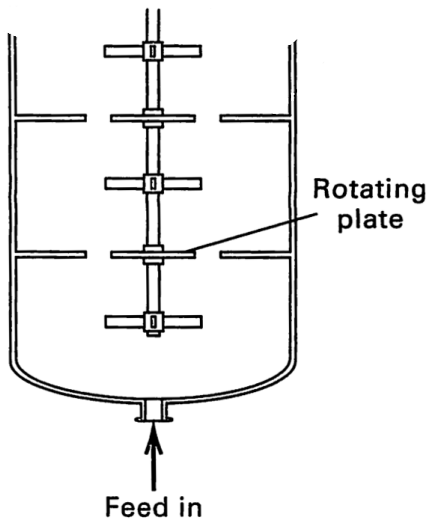[Seader, 3ed, p302]

Spray columns: separation principle is gravity
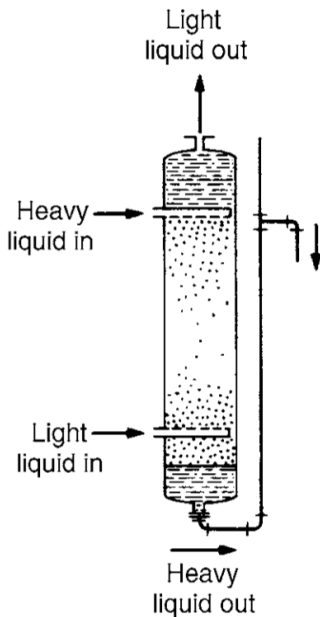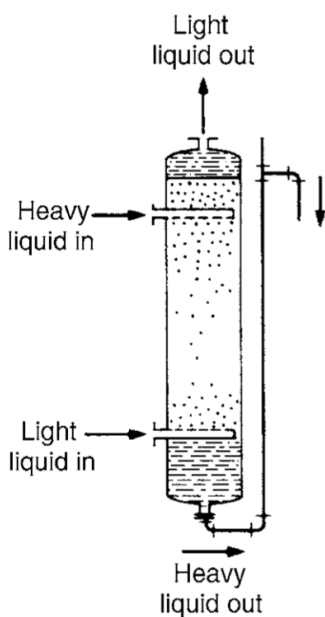
Tray columns

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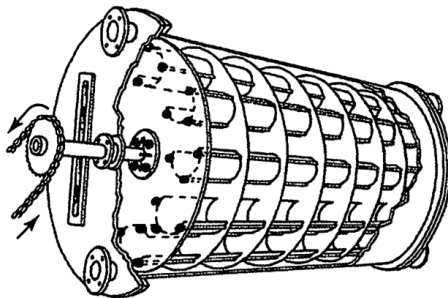- breaks gradient formation (axial dispersion)

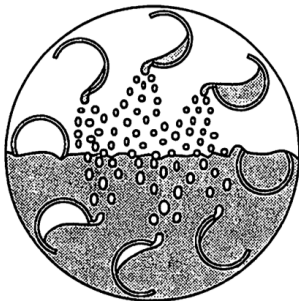# Tray columns with mechanical agitation

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

[Seader, 3ed, p302]

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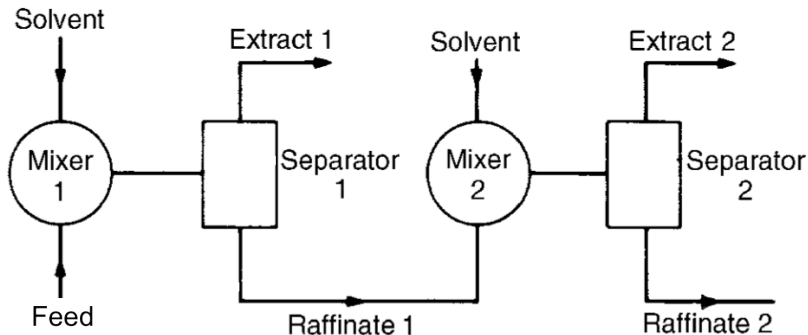
- ▶ "white" = lighter liquid
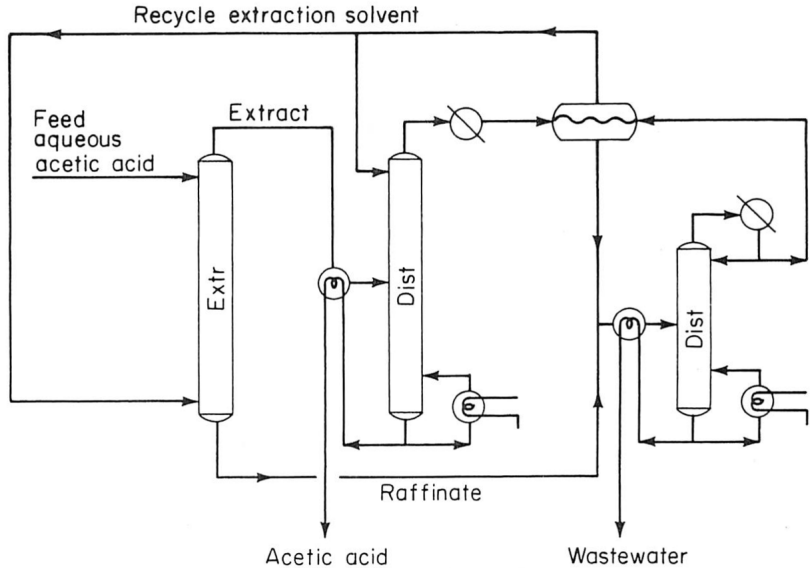- ▶ "grey" = heavier liquid

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

Dist

Raffinate

Acetic acid

Wastewater

[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:

$$F x_F + S y_S = E y_E + R x_R$$

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

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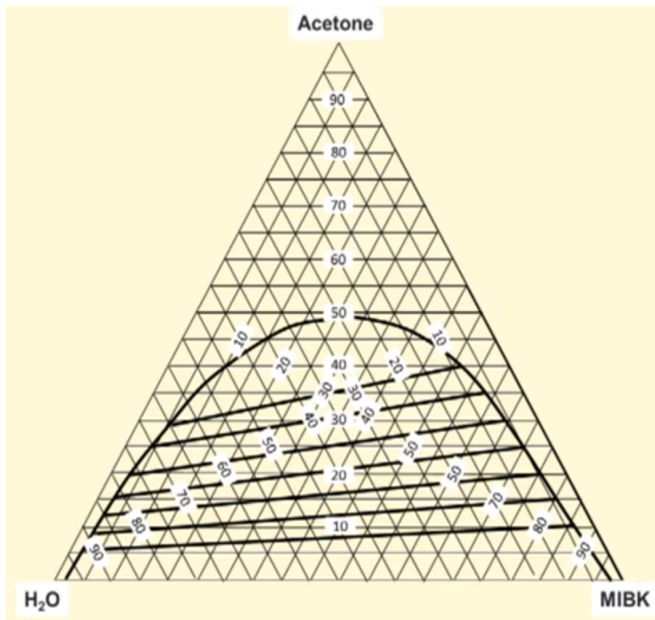
Also: see Perry's for many values of D
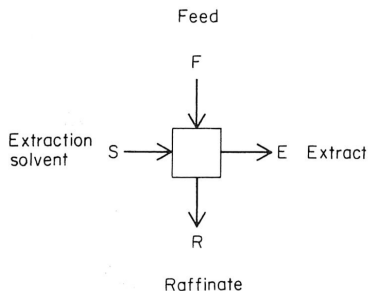
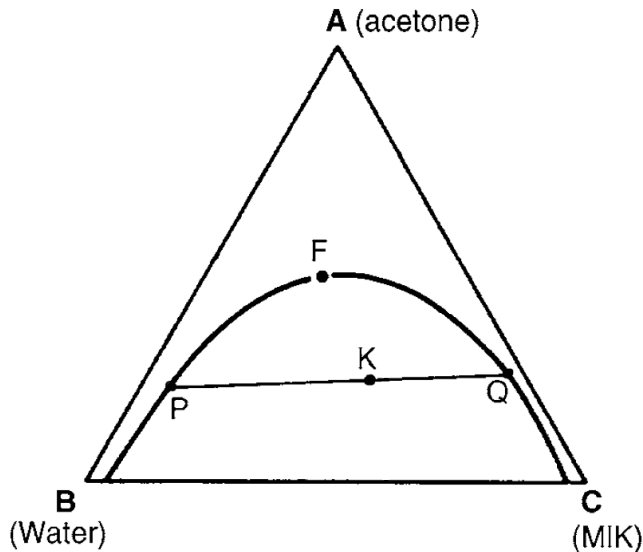# Triangular phase diagrams: from laboratory studies

Using a triangular phase diagrams
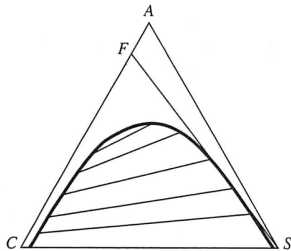
Lever rule

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: the range of feed concentrations (x_F) is wider, i.e. more
desirable, for (a). Difference between (a) and (b)

- ⬦ due to solvent choice
- ⬦ due to different temperatures
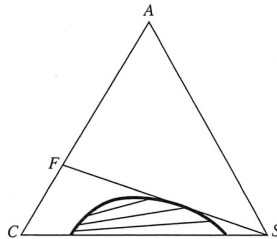- ⬦ due to pH modification, etc.

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)
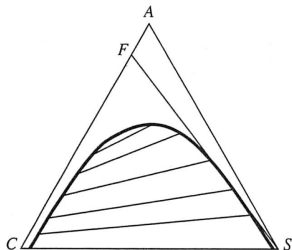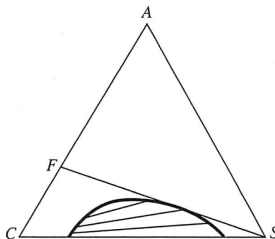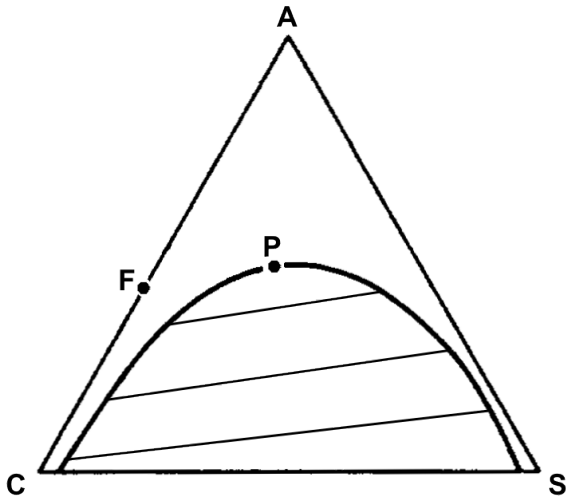

(a)   (b)

Answer: range of feed concentrations (x_F) is wider, i.e. more desirable, for **(a)**. Difference between (a) and (b):

- ▶ due to solvent choice
- ▶ due to different temperatures
- ▶ due to pH modification, *etc*
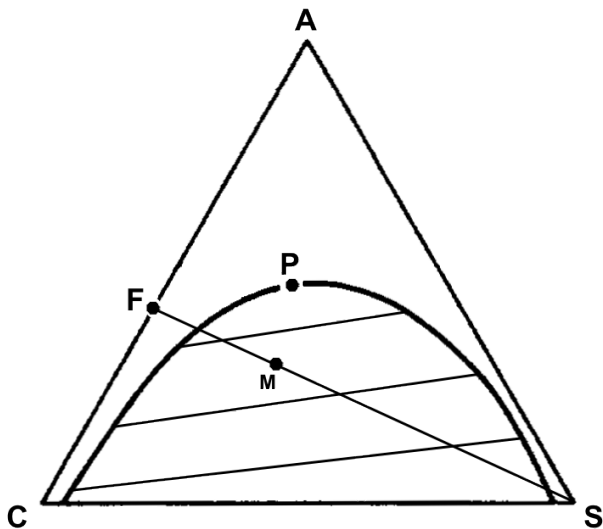
Q2: Using the lever rule

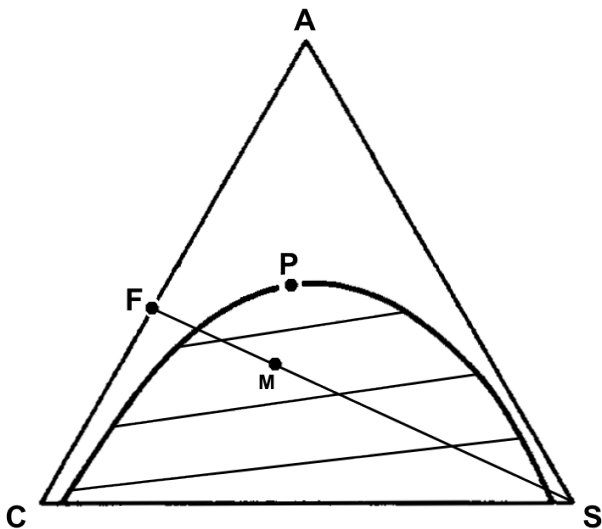Slide removed: was not a useful question

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?

Q3 *solution*: Using the lever rule
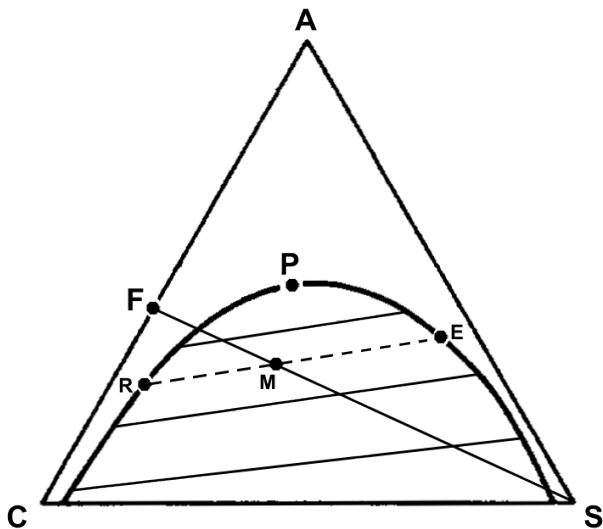

Composition of the mixture? Trick question: *we need more information* (e.g. amount of *F* **and** *S* must be given)
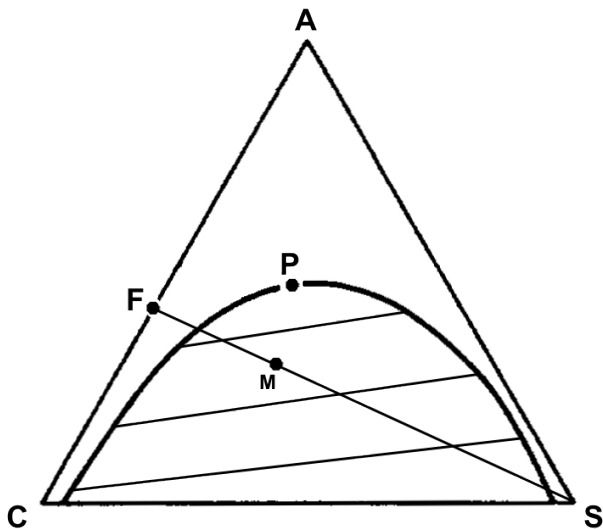
Let that mixture M achieve equilibrium. What is the composition of the raffinate and extract?

What is the composition of the raffinate and extract? *Use the tie lines* [solid lines]; *or interpolate between existing ones*.

Same system, but now lower solvent flow rate (to try save money!). What happens to (a) extract concentration and (b) solute recovery?

Q5 *solution*: Altering flows
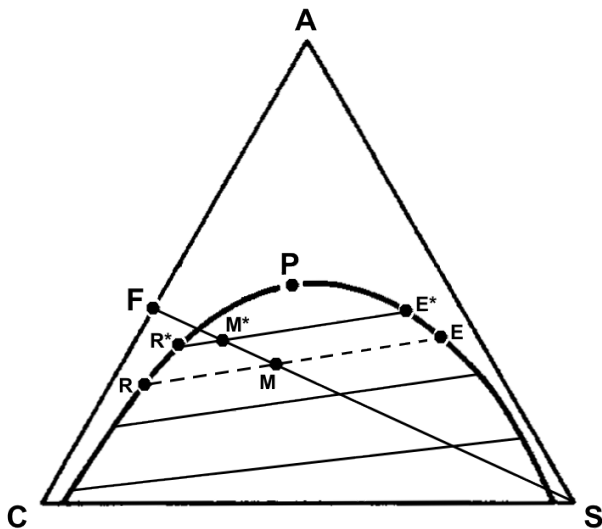
(a) *extract concentration increases*: (A at E*) > (A at E): $y_{E*} > y_E$

(b) *solute recovery drops*: (A at R*) > (A at R): $x_{R*} > x_R$

Q6: Composition of the mixture, M?

(Solute) A

Plait point

(Solvent) S — (Carrier) C

Feed

Solvent S → □ → E_1 Extract

R_1

Raffinate

--- Tie line
— Operating line
— Equilibrium curve
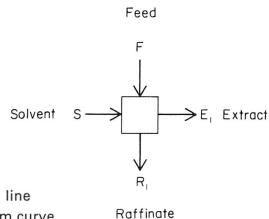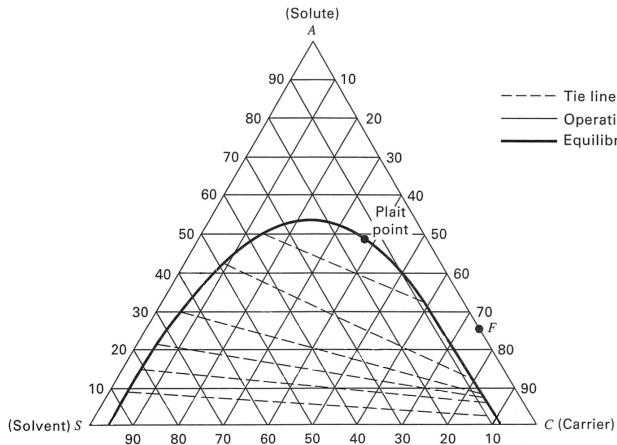
Feed	Solvent
$F = 250$ kg	$S = 100$ kg
$x_{F,A} = 0.24$	$x_{S,A} = 0.0$
$x_{F,C} = 0.76$	$x_{S,C} = 0.0$
$x_{F,S} = 0.00$	$x_{S,S} = 1.0$

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

Q6 *solution*: Composition of the mixture, M?

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

$$M = F + S$$
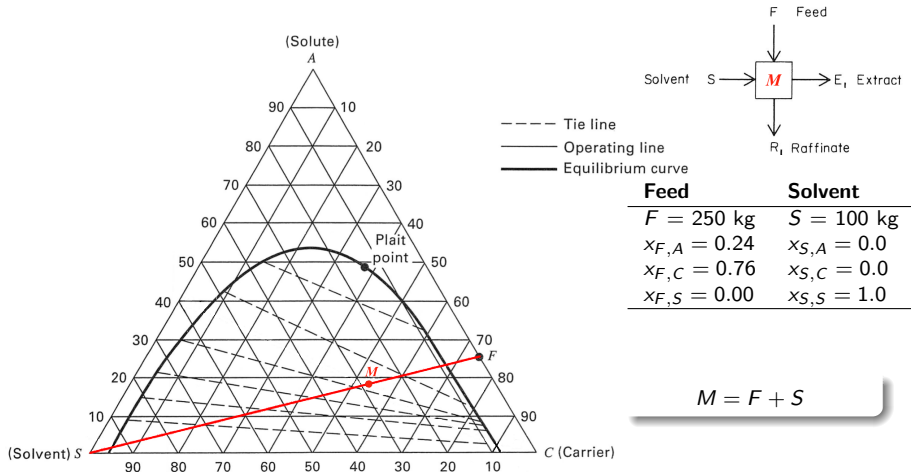
Answer: $M = 350$kg; $x_{M,A} = 0.17$; $x_{M,C} = 0.54$; $x_{M,S} = 0.29$

Q7: Composition of the 2 phases leaving in equilibrium?
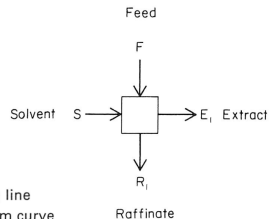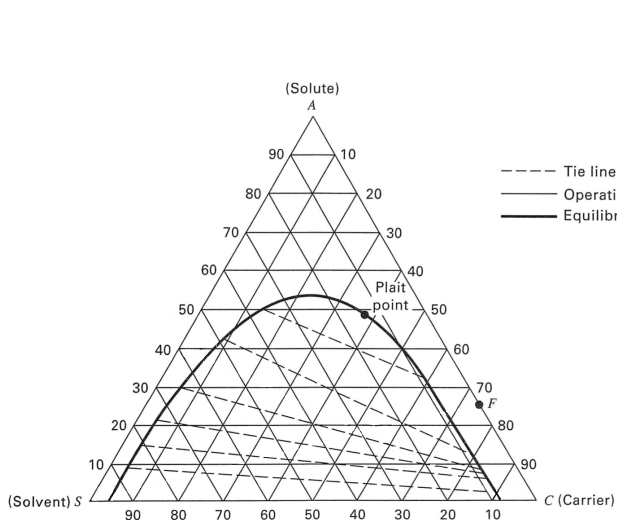
Feed	Solvent
$F = 250$ kg	$S = 100$ kg
$x_{F,A} = 0.24$	$x_{S,A} = 0.0$
$x_{F,C} = 0.76$	$x_{S,C} = 0.0$
$x_{F,S} = 0.00$	$x_{S,S} = 1.0$

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

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

Q7 *solution*: Composition of the 2 phases in equilibrium?
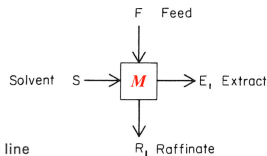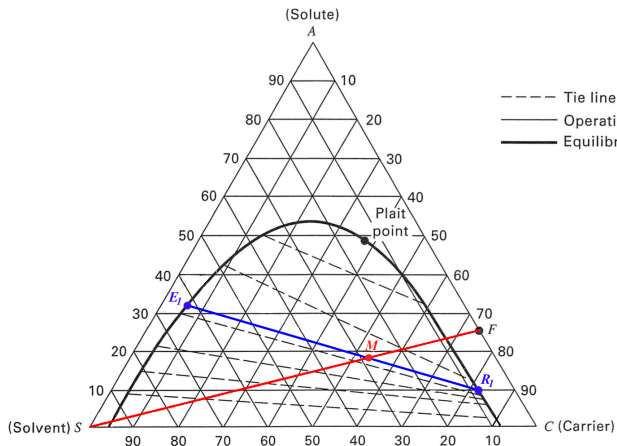
Feed / Solvent data:

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

$$M = E_1 + R_1$$

$R_1 = 222$kg; $\quad x_{R_1,A} = 0.10$; $\quad x_{R_1,C} = 0.82$; $\quad x_{R_1,S} = 0.08$

$E_1 = 128$kg; $\quad x_{E_1,A} = 0.33$; $\quad x_{E_1,C} = 0.06$; $\quad x_{E_1,S} = 0.61$
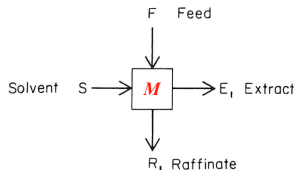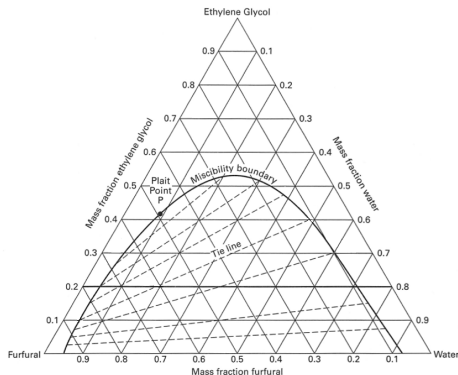
Phase diagram: furfural, water, ethylene glycol

Feed	Solvent
$F = 100$ kg	$S = 200$ kg
$x_{F,A} = 0.45$	$x_{S,A} = 0.0$
$x_{F,C} = 0.55$	$x_{S,C} = 0.0$
$x_{F,S} = 0.00$	$x_{S,S} = 1.0$

- ► A = ethylene glycol (solute)
- ► C = water (carrier)
- ► S = furfural (solvent)

AIM: to remove ethylene glycol (solute) from water (carrier) into solvent (furfural)

1. Calculate the mixture composition, M
2. Calculate the equilibrium compositions in E_1 and R_1

Note: extract is defined as "the solvent-rich stream leaving the system"

Ethylene Glycol

Mass fraction ethylene glycol

Mass fraction water

Miscibility boundary

Plait Point P

Tie line

F

R_1

E_1

M

Furfural

Mass fraction furfural

Water

37
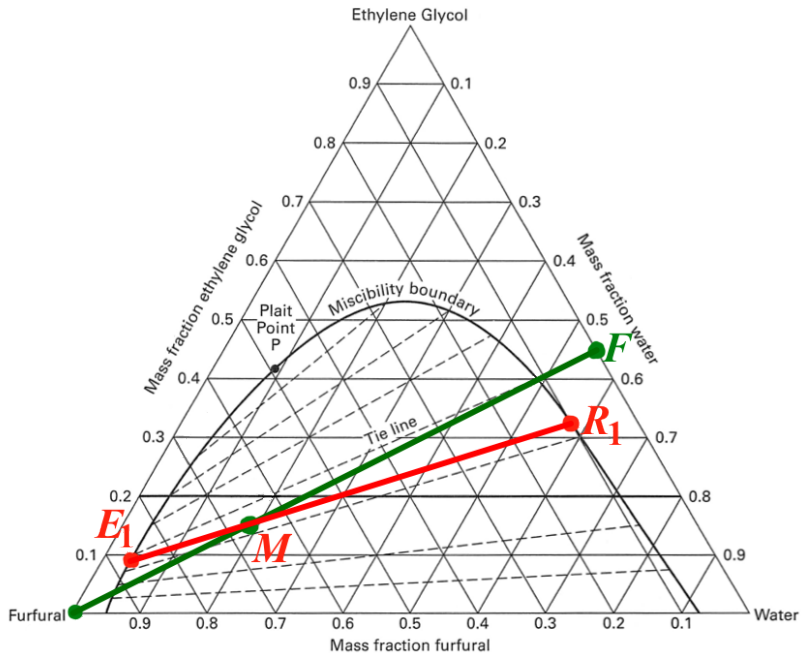
Solution: Phase diagram: furfural, water, ethylene glycol

Feed	Solvent
$F = 100$ kg	$S = 200$ kg
$x_{F,A} = 0.45$	$x_{S,A} = 0.0$
$x_{F,C} = 0.55$	$x_{S,C} = 0.0$
$x_{F,S} = 0.00$	$x_{S,S} = 1.0$

- A = ethylene glycol solute
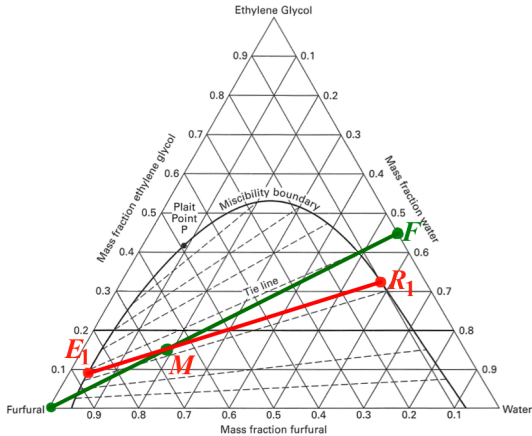- C = water (carrier)
- S = furfural solvent

$M = 300$kg; $x_{M,A} = 0.15$; $x_{M,C} = 0.18$; $x_{M,S} = 0.67$
$R_1 = 82$kg; $x_{R_1,A} = 0.33$; $x_{R_1,C} = 0.57$; $x_{R_1,S} = 0.10$
$E_1 = 218$kg; $x_{E_1,A} = 0.09$; $x_{E_1,C} = 0.04$; $x_{E_1,S} = 0.87$

Link units in *series*
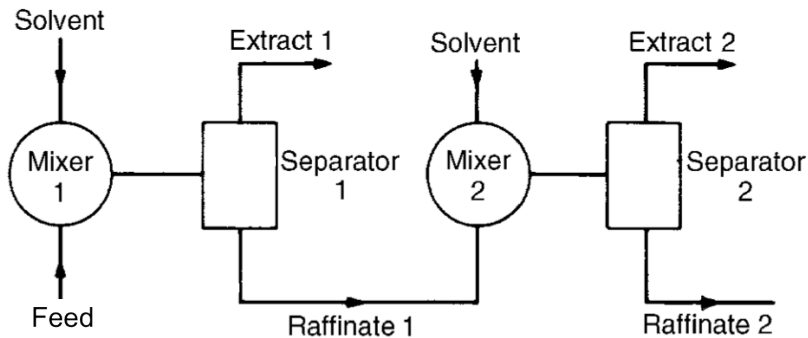
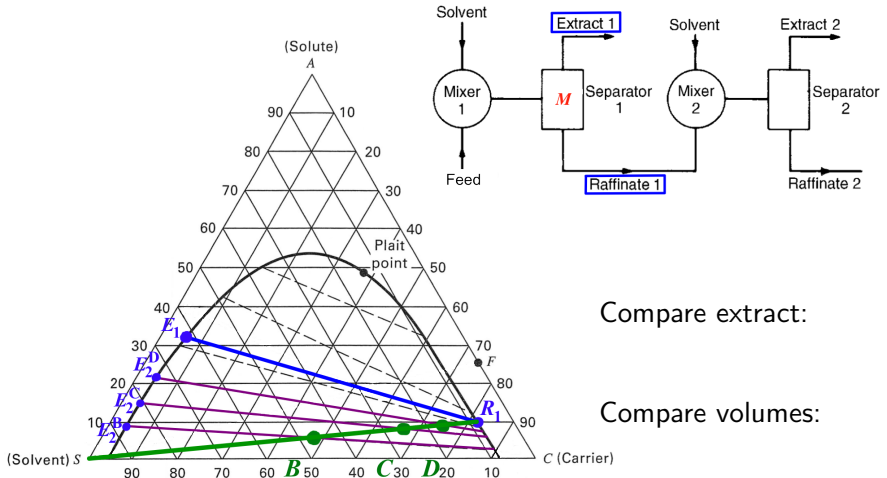[Richardson and Harker, p 723]

Q8: send raffinate from Q7 to second mixer-settler
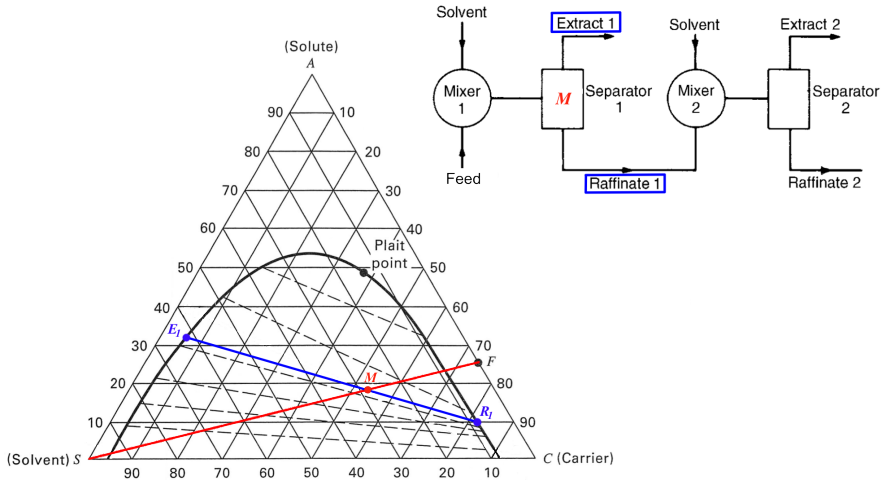
Question: how much solvent should we use in the second stage?

Q8 *solution*: send raffinate from Q7 to second mixer-settler

Compare extract:

Compare volumes:

Answer: equilibrium from point B (most solvent), C, D (least solvent) will each be different. Trade-off: higher extraction vs lower recovery

Course project

For the final report:

- Please give a flowsheet of the overall process
- Only focus on 1 separation unit operation
- Some groups have 2 or 3 separation steps: only 10 pages!
- You must focus on the **separation** step in the flowsheet
- Provide a detailed drawing of the unit
- You must show the detailed design calculation for **sizing** the unit
- Choose a basis for sizing: e.g.
    - based on the inlet requirement(s), or
    - based on the outlet requirement(s)
- Brief discussion on capital costs and annual operating costs
    - maintenance
    - ESA and/or MSA requirements

Report's length

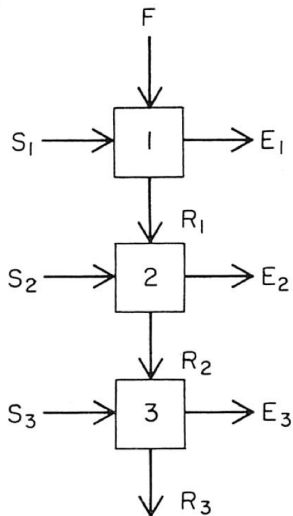10 pages maximum, please see course website

Administrative issues: dates

Unit	Previous date	Revised date
Assignment 4	01 November	06 November
Project report	09 November	16 November
Assignment 5	16 November	23 November
Take-home exam	30 November	30 November

Series of co-current units

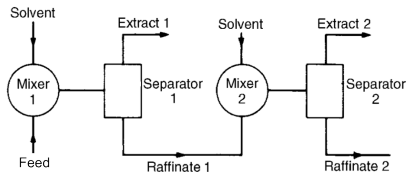$N = 3$ in this illustration

▶ Recovery = fraction of solute recovered

$$1 - \frac{(x_{R_N})(R_N)}{(x_F)(F)}$$

▶ Concentration of overall extract = solute leaving in each extract stream, divided by total extract flow rate
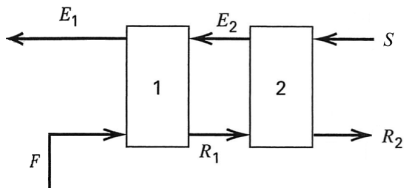
$$\frac{\sum\limits_{n}^{N} (y_{E_n})(E_n)}{\sum\limits_{n}^{N} E_n}$$

Co-current *vs* counter-current

Co-current ($N = 2$ stages)

Counter-current ($N = 2$ stages)

- We combine multiple extract streams
- (Only 2 in illustration)
- In general: $y_{E_1} > y_{E_2} > \ldots$
- Fresh solvent added at each stage

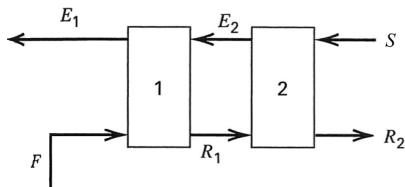- "Re-use" the solvent, so
- Far lower solvent flows
- Recovery $= 1 - \dfrac{(x_{R_N})(R_N)}{(x_F)(F)}$
- Concentration $= y_{E_1}$

You will have an assignment question to compare and contrast these two configurations

Some theory: Two *counter-current* units

Just **consider** $N = 2$ **stages** for now. Steady state mass balance:

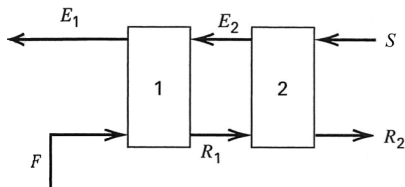$$F + E_2 = E_1 + R_1 \qquad\qquad E_2 + R_2 = S + R_1$$

Rearrange:

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

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

Note: each difference is equal to P (look on the flow sheet where those *differences* are).

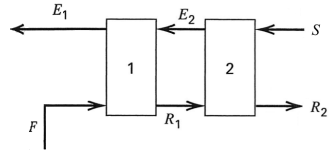# Counter-current graphical solution: 2 units

Rearranging again:
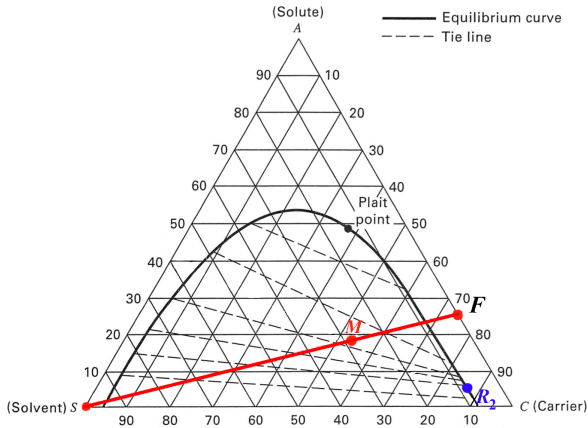
$$F + P = E_1$$
$$R_1 + P = E_2$$
$$R_2 + P = S$$

Interpretation: P **is a fictitious operating point on the ternary diagram** (from lever rule)
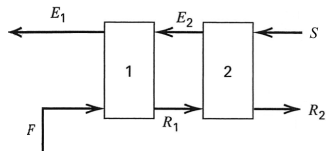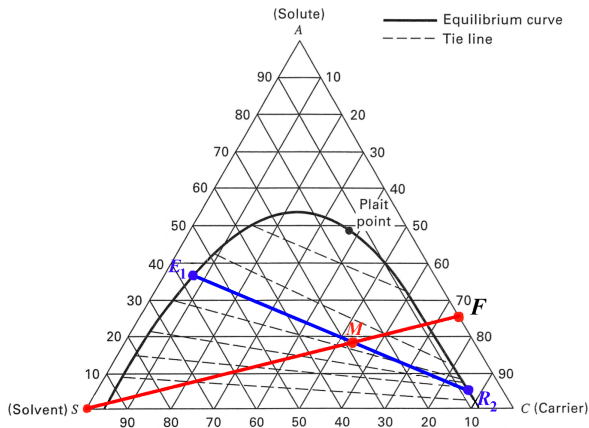
- P connects F and E_1
- P connects R_1 and E_2
- P connects R_2 and S

Counter-current graphical solution: 2 units

For example, let's require $x_{R_2,A} = 0.05$ (solute concentration in raffinate).
What is $y_{E_1,A}$ then (concentration of solute in the extract)?
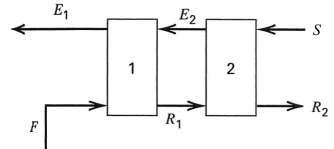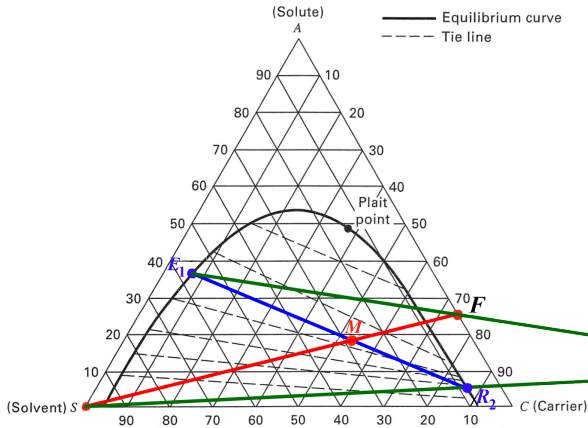
Counter-current graphical solution: 2 units

Note: the line connecting E_1 to R_2 **is not a tie line**. We use the lever rule and an overall mass balance ($F + S = E_1 + R_2$) to solve for all flows and compositions of $F, S, E_1,$ and R_2.

$y_{E_1,A} \approx 0.38$ is found from an overall mass balance, through M.

Counter-current graphical solution: 2 units
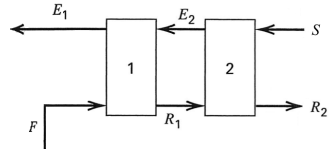

Recall:

$$F + P = E_1$$

$$R_2 + P = S$$

Extrapolate through these lines until intersection at point P.

Minimal achievable E_1 concentration? *mentally move point M towards S*.
What happens to P? Alternative (simpler?) explanation on next slide.

Counter-current graphical solution: maximum solvent flow
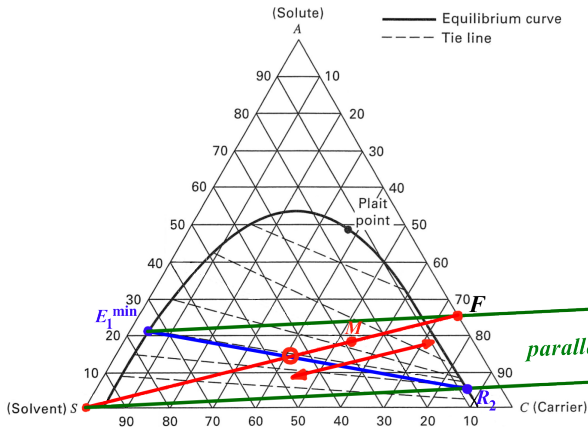
Recall:

$$F + P = E_1$$

$$R_2 + P = S$$

parallel lines

Subtle point: minimal achievable E_1^{min} concentration:
- occurs at a certain *maximum* solvent flow rate indicated by ⚪
- note that R_2 is fixed (specified) in this example

Counter-current graphical solution: 2 units
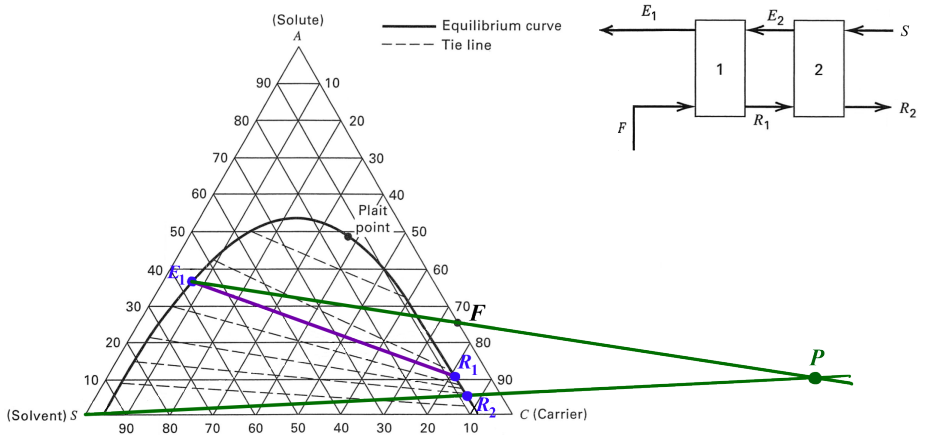
Once we have E_1, we can start: note that in stage 1 the R_1 and E_1 streams leave in equilibrium and can be connected with a tie line.

Counter-current graphical solution: 2 units
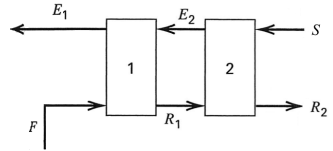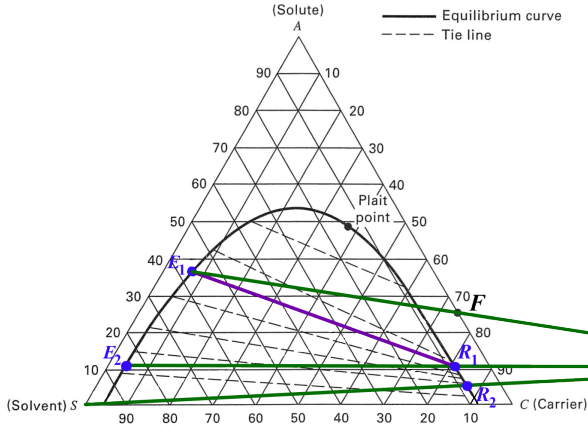
Again recall:
$$R_1 + P = E_2$$

Since we have point P and R_1 we can bring the operating line back and locate point E_2

Counter-current graphical solution: 2 units

The last unit in a cascade is a special case: we already know $R_{N=2}$, but we could have also calculated it from the tie line with E_2. We aim for some overshoot of R_N. (Good agreement in this example.)

In general: *Counter-current* units

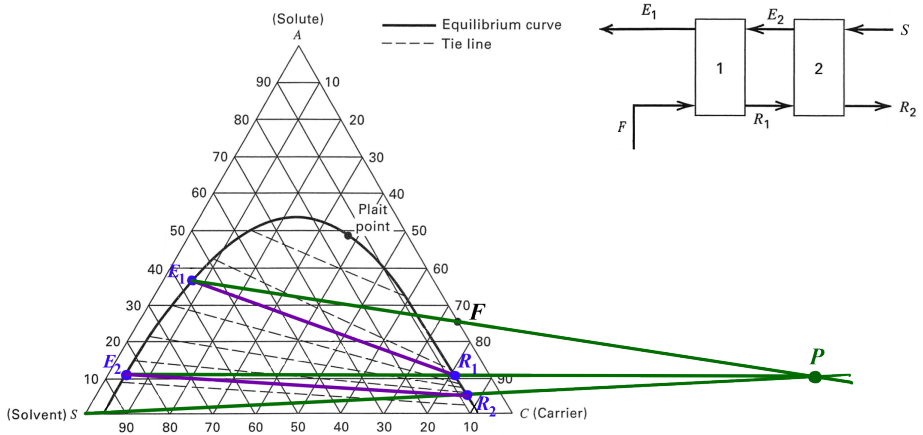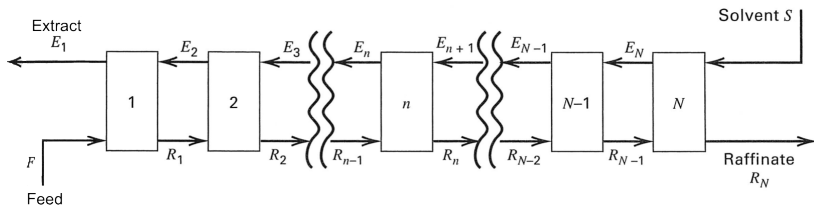$$F + E_2 = E_1 + R_1 \qquad E_2 + R_2 = E_3 + R_1 \qquad E_n + R_n = E_{n+1} + R_{n-1}$$

Rearrange:

$$F - E_1 = R_1 - E_2 \qquad R_1 - E_2 = R_2 - E_3 \qquad R_{n-1} - E_n = R_n - E_{n+1}$$

$$(F - E_1) = (R_1 - E_2) = \ldots = (R_{n-1} - E_n) = (R_n - E_{n+1}) = \ldots = (R_N - S) = \mathbf{P}$$

Notes:
1. each difference is equal to P (the difference between flows)
2. E_n and R_n are in equilibrium, leaving each stage [via tie line]

Counter-current graphical solution
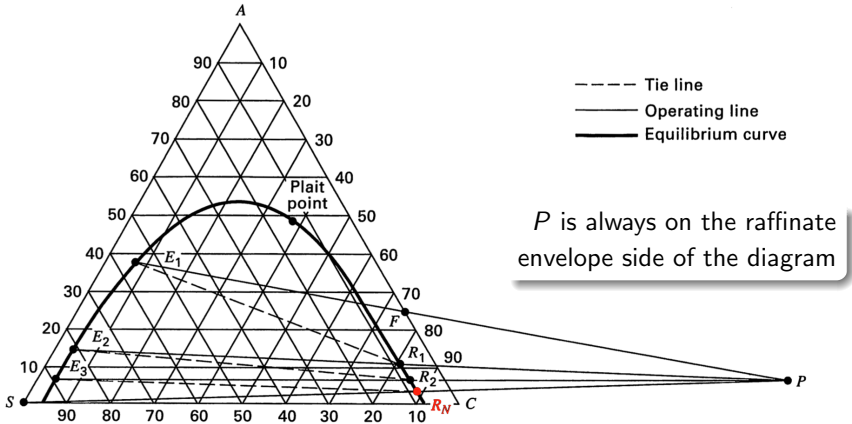

> P is always on the raffinate envelope side of the diagram

1. We know F and S; connect with a line and locate "mixture" M

2. Either specify E_1 or R_N (we will always know one of them)

3. Connect a straight line through M passing through the one specified

4. Solve for unspecified one [via tie line]

5. Connect S through R_N and extrapolate

6. Connect E_1 through F and extrapolate; cross lines at P

7. Locate P by intersection of 2 lines

8. In general: connect E_n and R_n via equilibrium tie lines

Relating the theoretical stages to an actual unit

Assume we calculated $N \approx 6$, for example, as the theoretical stages required:

Note:

- ▶ does not mean we require 6 mixer-settlers (though we could do that, but costly)
- ▶ it means we need a **column** which has equivalent operation of 6 counter-current mixer-settlers that fully reach equilibrium
- ▶ at this point we resort to correlations and vendor assistance

Tutorial-style question

> Consider a system for which you have been given the ternary diagram (see next slides). A = solute, S = solvent, C = carrier. The feed, F enters at 112 kg/hr with composition of 25 wt% solute and 75 wt% carrier.

1. Calculate the flow and composition of the extract and raffinate from:
   - 1st co-current stage, using a pure solvent flow of 50 kg/hr.
   - 2nd co-current stage, with an additional solvent flow of 50 kg/hr.
2. For the overall 2-stage system, find the:
   - overall recovery [*answer:* ~93%]
   - overall concentration of combined extract streams [*answer:* ~21%]
3. The objective now is to have a counter-current system so the raffinate leaving in the Nth stage, R_N has $y_{R_N} = 0.025$
   - What is the *maximum allowable solvent flow*?
   - Explain whether it's possible to achieve an extract stream of $y_{E_1} = 0.21$?
   - Show the construction on the ternary diagram for the number of equilibrium stages to achieve $y_{R_N} = 0.025$, given a solvent flow of 60 kg/hr.
   - Plot on the same axes the concentrations in the extract and raffinate streams.

For practice
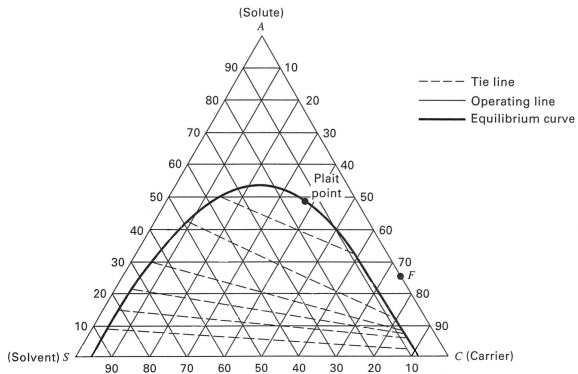
For practice
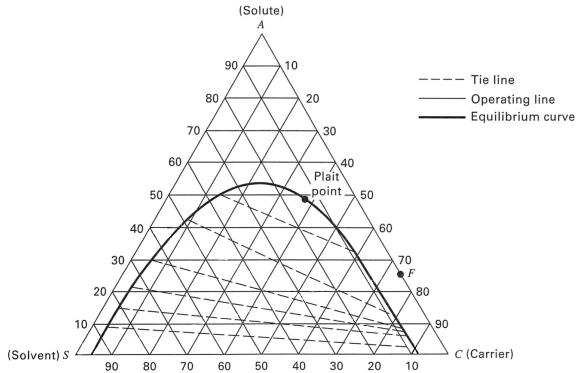
References

- 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