# Separation Processes

## ChE 4M3



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Overall revision number: 95 (October 2012)

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# Liquid-liquid extraction (LLE)

[Flickr# 3453475667]

# 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*?

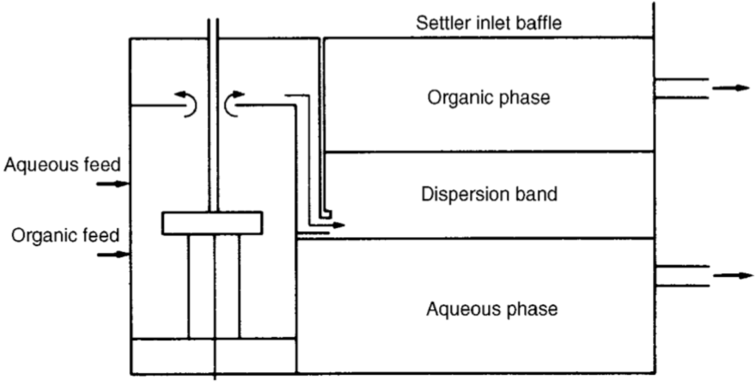
- Counter-current mixer-settlers in series
- High interfacial area during mixing
- Reduce mass-transfer resistance
- Promote mass transfer
  - molecular diffusion
  - eddy diffusion $\leftarrow$ orders of magnitude greater

# 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 $\mu$m
   - 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).

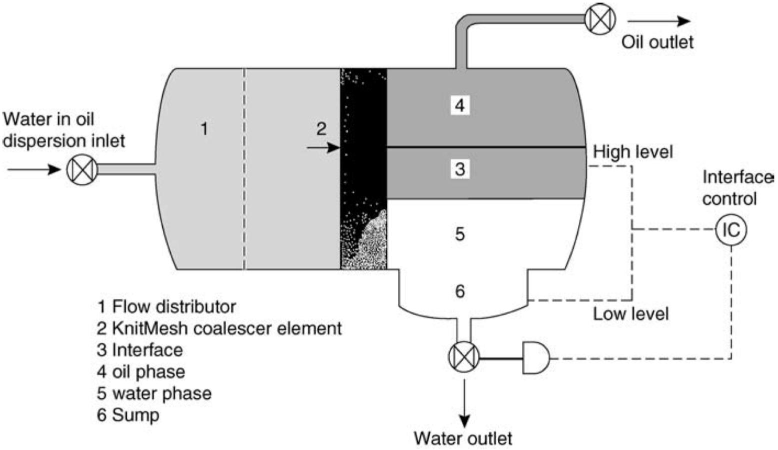
# Mixer-settlers




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

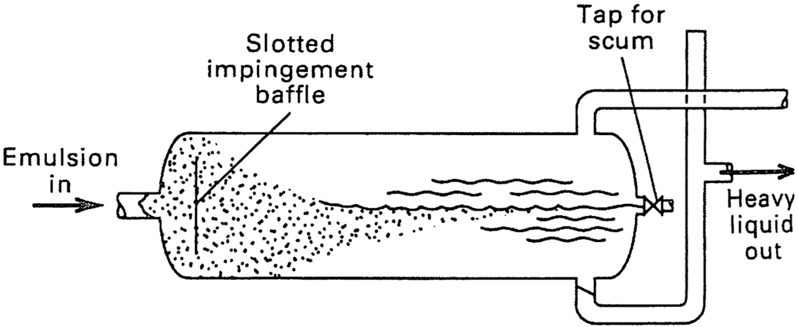
# Mixer-settlers

KnitMesh coalescer: consistency of “steel wool”



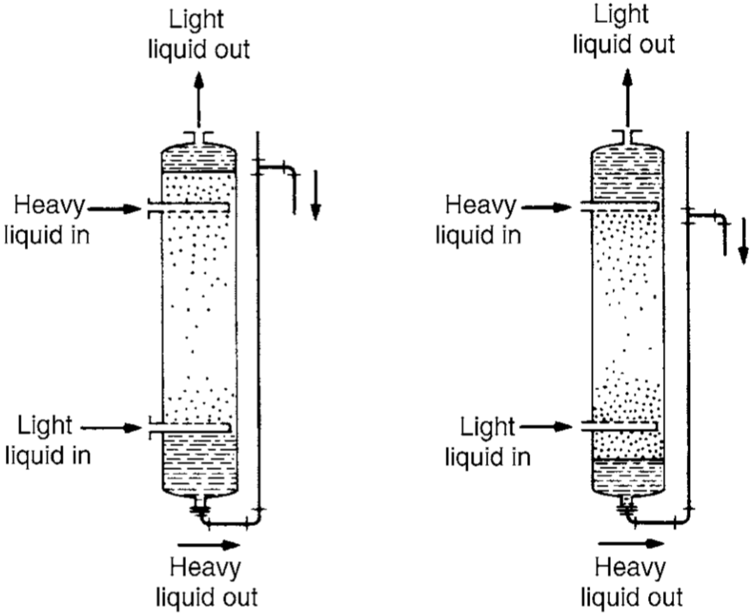

[Richardson and Harker, p 747]

# Horizontal gravity settling vessel



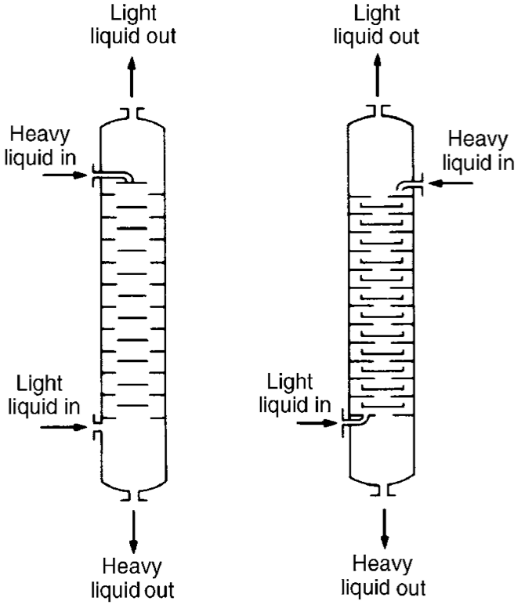

[Seader, 3ed, p302]

# Spray columns: separation principle is gravity




[Richardson and Harker, p 751]

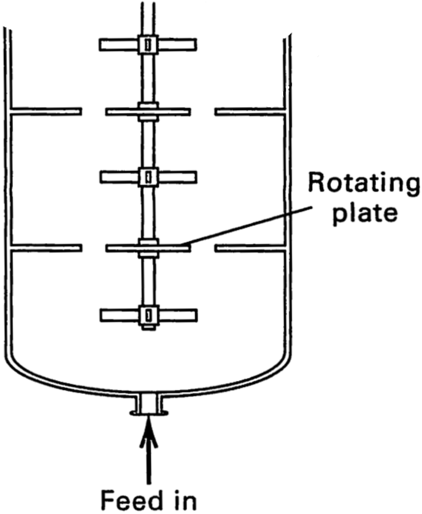
# Tray columns




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

[Richardson and Harker, p 749]

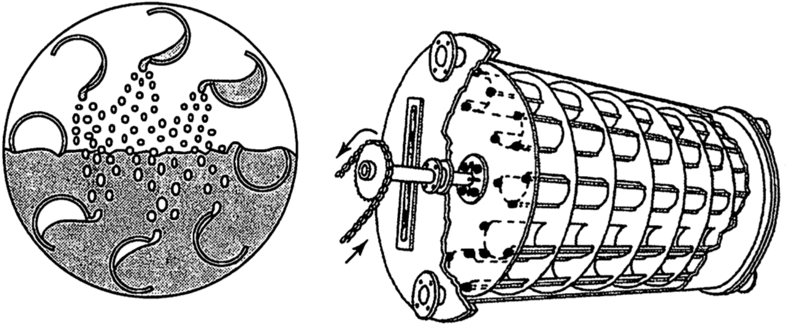
# Tray columns with mechanical agitation




[Seader, 3ed, p302]

- shearing to create dispersion
- can have alternating layers of packing (coalescence)
- some column designs pulsate $\Uparrow\Downarrow$

# Rotating devices

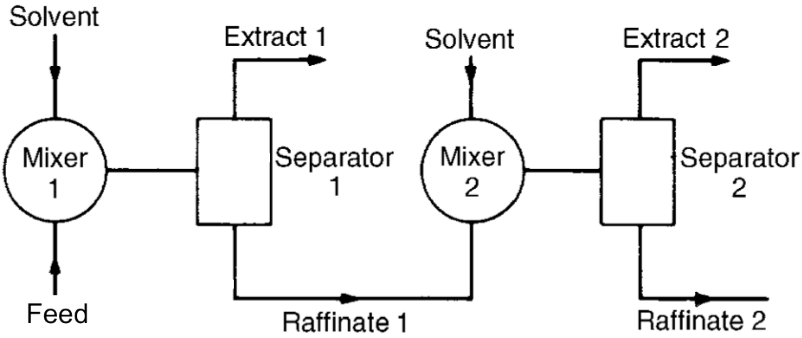


[Seader, 3ed, p 306]

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

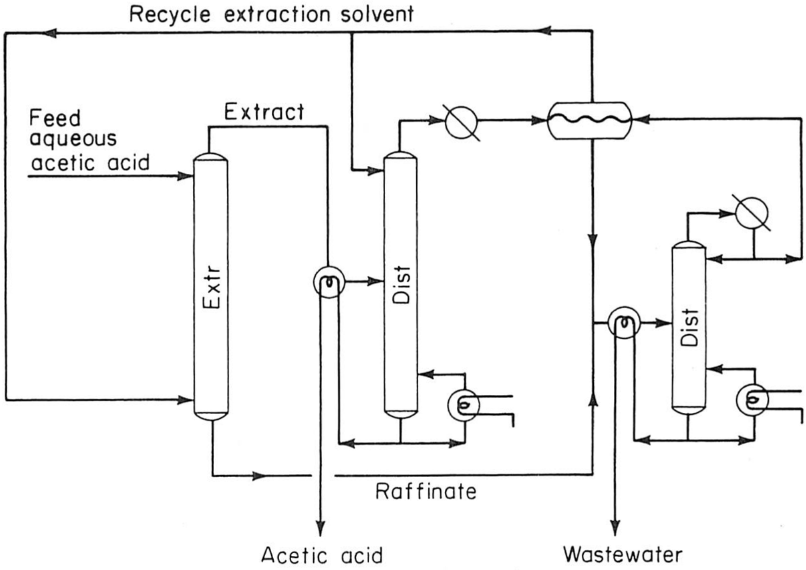
Used when foams and emulsions would easily form: i.e. gentle mass transfer.

# Linking up units (more on this later)




[Richardson and Harker, p 723]

# Integration with downstream units




[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?

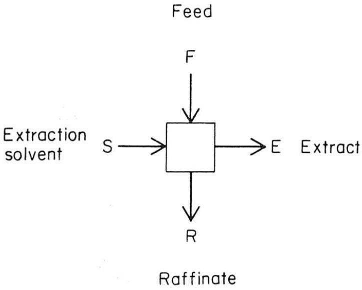
- High distribution coefficient (selectivity) for solute
- Low distribution coefficient for carrier
- Reasonable volatility difference with solute and carrier
- Reasonable surface tension: easy to disperse **and** coalesce
- High density difference: separates rapidly by gravity
- Stability to maximize 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 $x_R$:

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

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

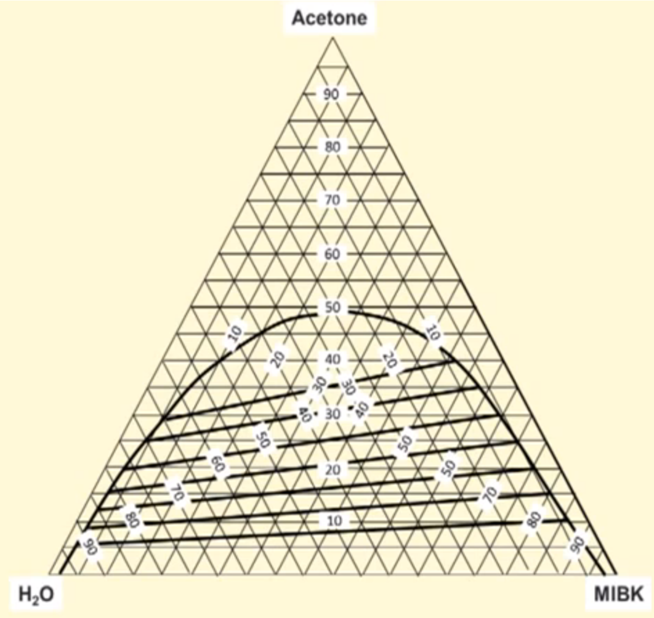
Once $D$ is determined, we can obtain phase diagrams to understand how the process will operate.

Also: see Perry's for many values of $D$

# Triangular phase diagrams: from laboratory studies

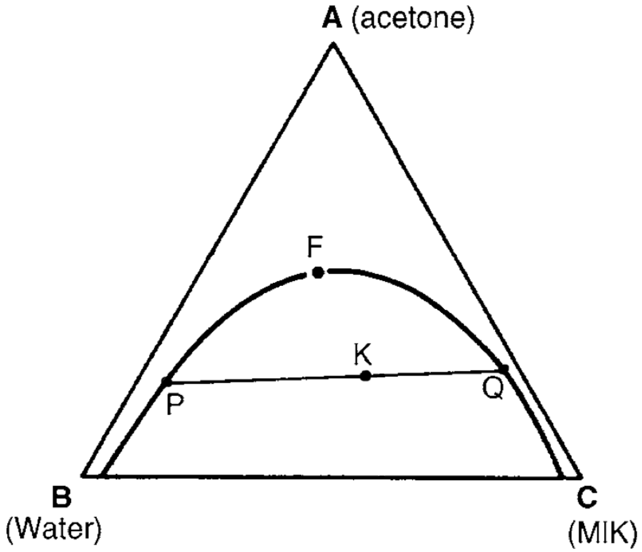
[Flickr# 3453475667]

# Using a triangular phase diagrams




[http://www.youtube.com/watch?v=gGYHXhcKM5s]

# Lever rule



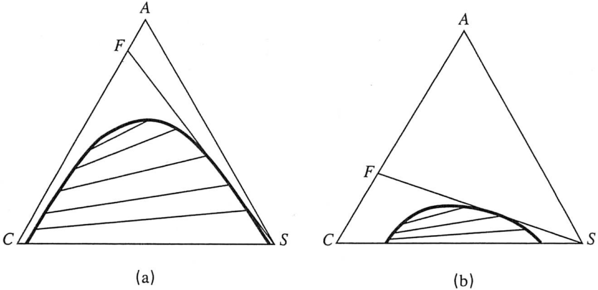

**Mix P and Q**

- 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 $x_F$)




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*

# Q1: Using the lever rule

Which is a more *flexible* system?

- S = pure solvent used
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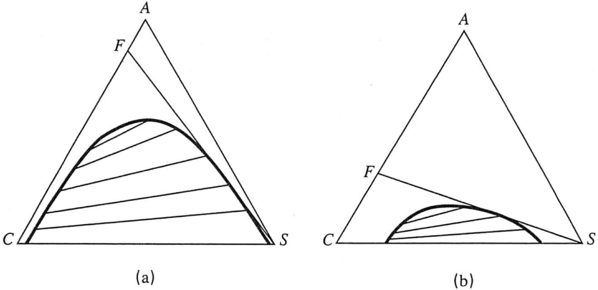
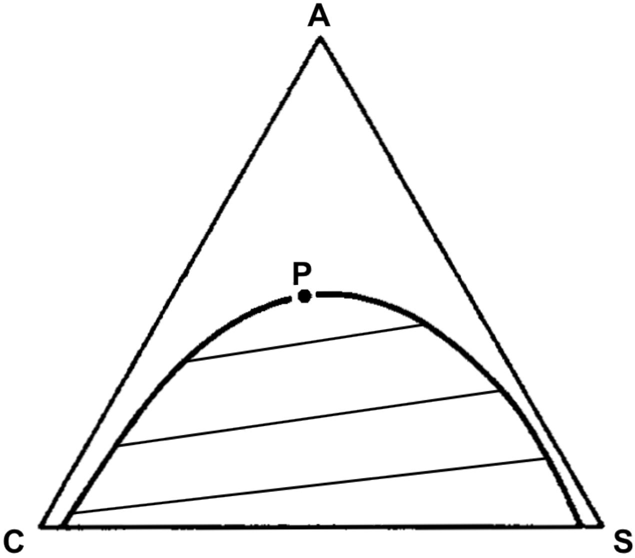



Answer: range of feed concentrations ($x_F$) is wider, i.e. more desirable, for **(a)**. Difference between (a) and (b):

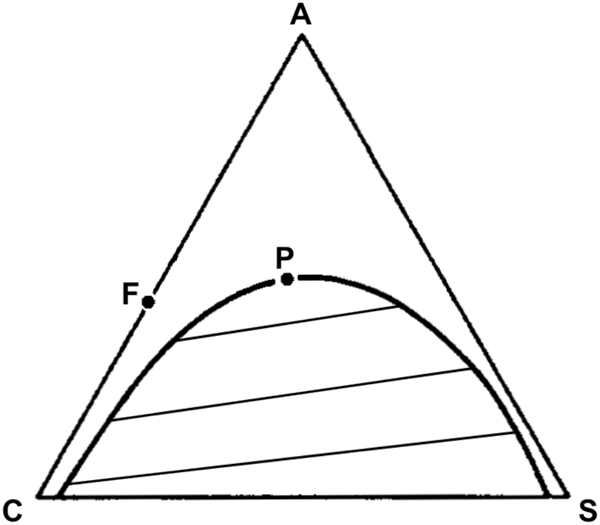
- due to solvent choice
- due to different temperatures
- due to pH modification, *etc*

# Q2: Using the lever rule



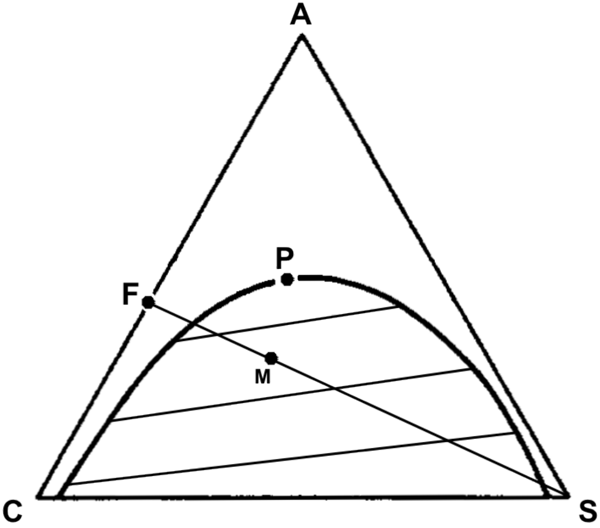

Which is a more effective as a solvent: C or S ?

# Q3: Using the lever rule



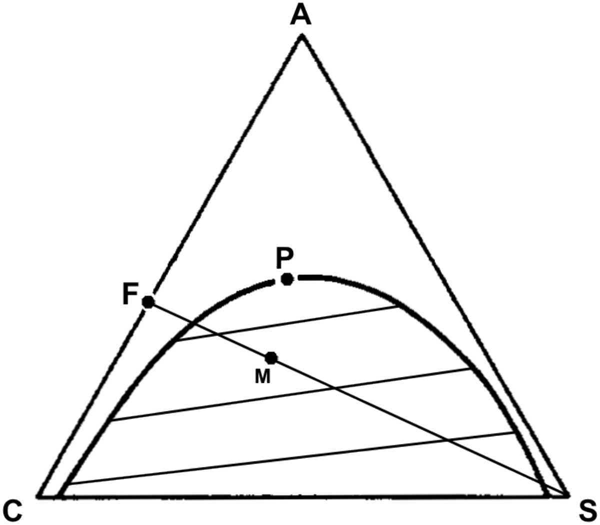

Mix a feed stream, $F$, containing $C$ and $A$ (i.e. $x_F$) with a pure solvent stream $S$ (i.e. $y_S = 0$). Composition of the mixture?

# Q3 *solution*: Using the lever rule



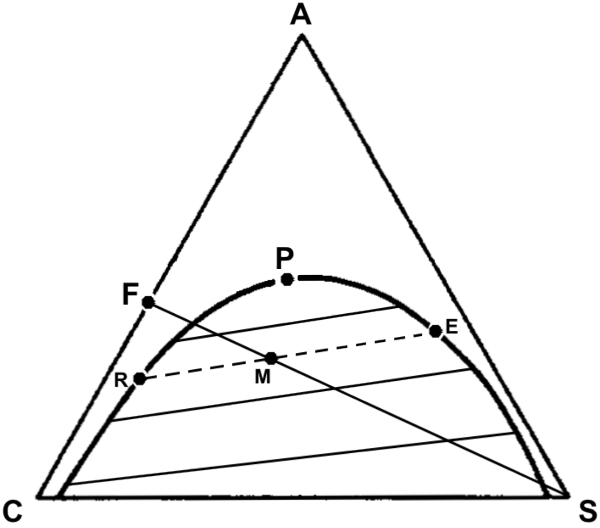

Composition of the mixture? Trick question: *we need more information* (e.g. amount of $F$ **and** $S$ must be given)

# Q4: Going to equilibrium



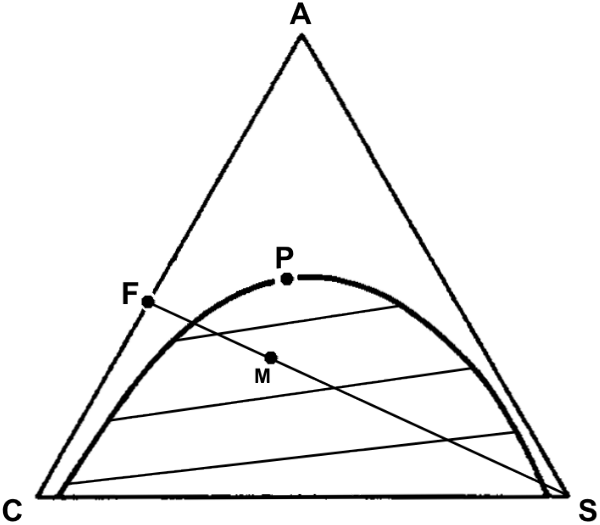

Let that mixture $M$ achieve equilibrium. What is the composition of the raffinate and extract?

# Q4 *solution*: Going to equilibrium



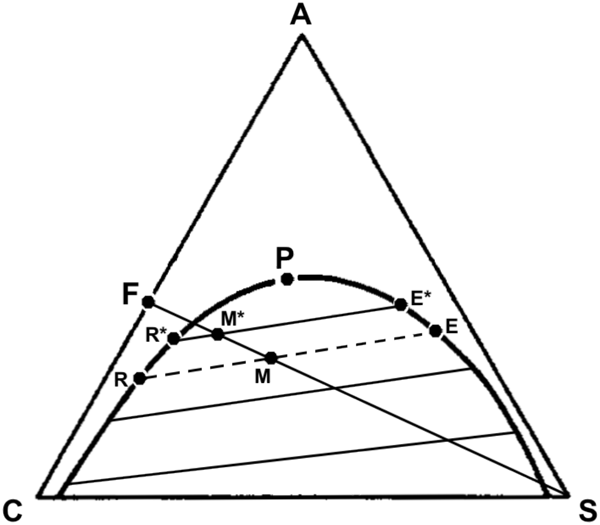

What is the composition of the raffinate and extract? *Use the tie lines* [solid lines]; *or interpolate between existing ones*.

# 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?

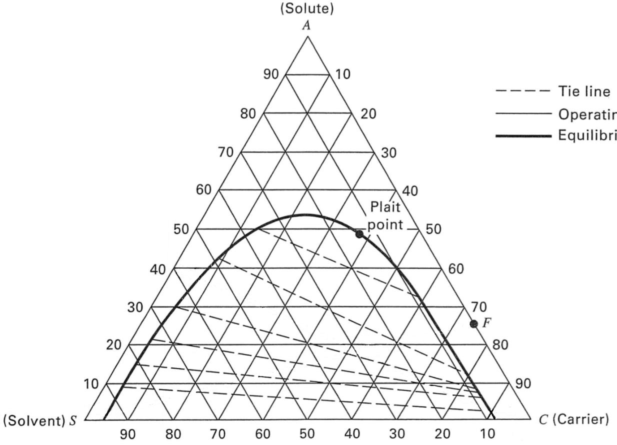
# Q5 *solution*: Altering flows

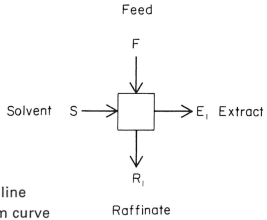



(a) *extract concentration increases*: (A at E*) $>$ (A at E): $y_{E^*} > y_E$

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

# Q6: Composition of the mixture, $M$?

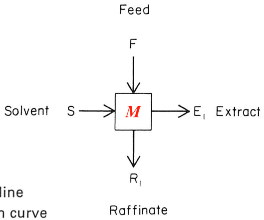


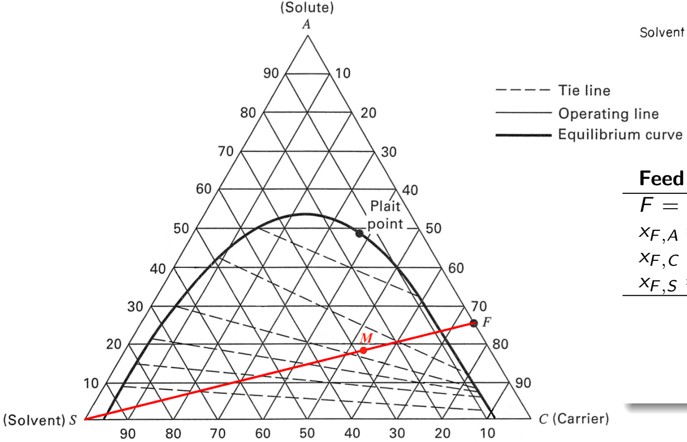




| **Feed** | **Solvent** |
|---|---|
| $F = 250$ kg | $S = 100$ kg |
| $x_{F,A} = 0.24$ | $x_{S,A} = 0.0$ |
| $x_{F,C} = 0.76$ | $x_{S,A} = 0.0$ |
| $x_{F,S} = 0.00$ | $x_{S,A} = 1.0$ |

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

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




| **Feed** | **Solvent** |
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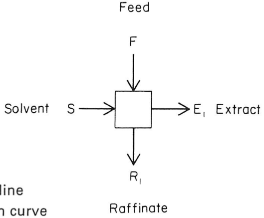
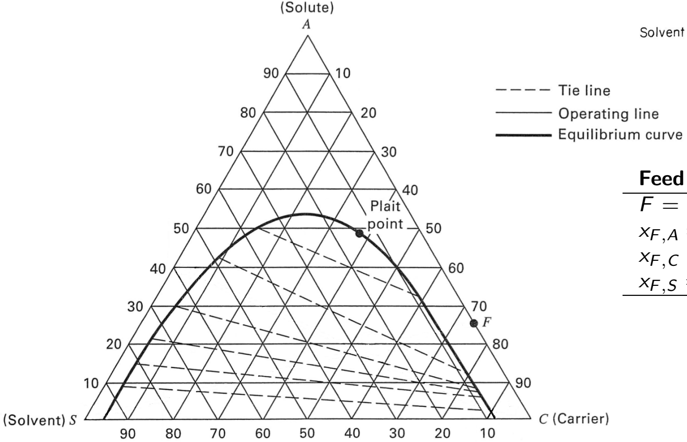
| $x_{F,C} = 0.76$ | $x_{S,A} = 0.0$ |
| $x_{F,S} = 0.00$ | $x_{S,A} = 1.0$ |

$$M = F + S$$

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?



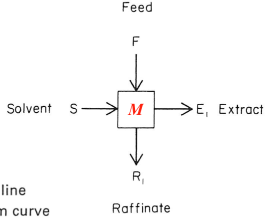



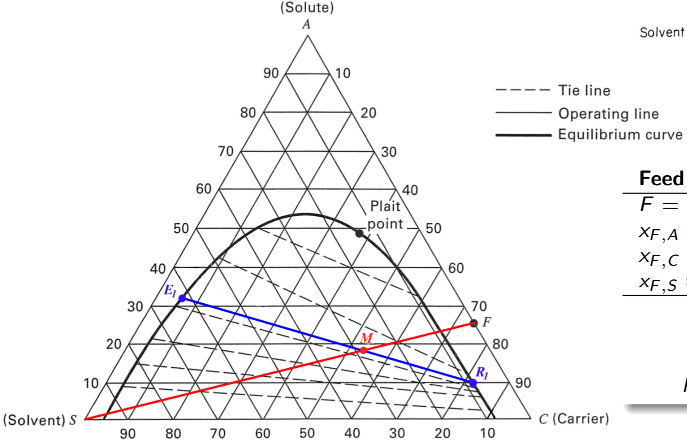

| Feed | Solvent |
|---|---|
| $F = 250$ kg | $S = 100$ kg |
| $x_{F,A} = 0.24$ | $x_{S,A} = 0.0$ |
| $x_{F,C} = 0.76$ | $x_{S,A} = 0.0$ |
| $x_{F,S} = 0.00$ | $x_{S,A} = 1.0$ |

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

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

# Q7 *solution*: Composition of the 2 phases in equilibrium?




| **Feed** | **Solvent** |
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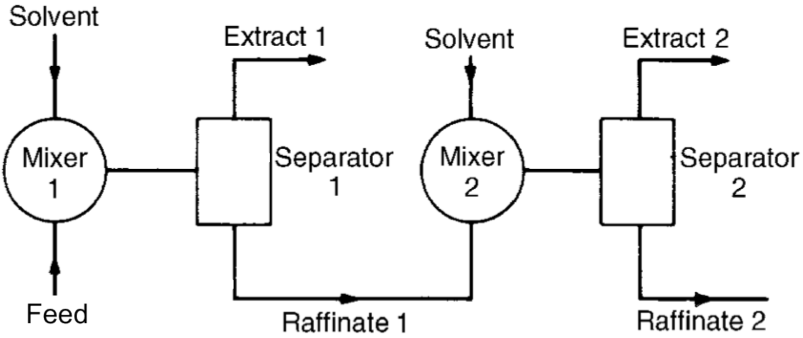
| $x_{F,C} = 0.76$ | $x_{S,A} = 0.0$ |
| $x_{F,S} = 0.00$ | $x_{S,A} = 1.0$ |

$$M = E_1 + R_1$$

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

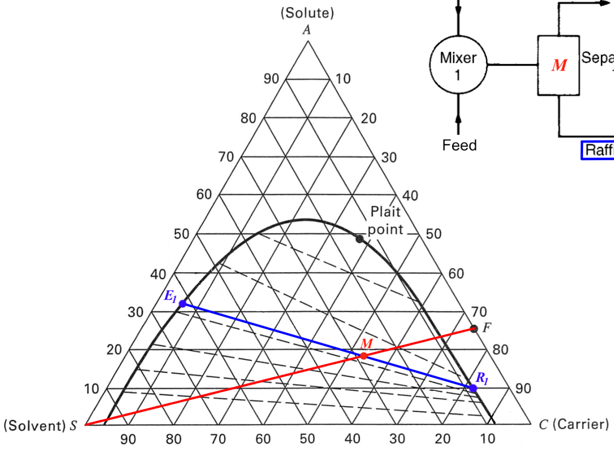
$$E_1 = 128\text{kg}; \quad x_{E_1,A} = 0.33; \quad x_{E_1,C} = 0.06; \quad x_{E_1,S} = 0.61$$

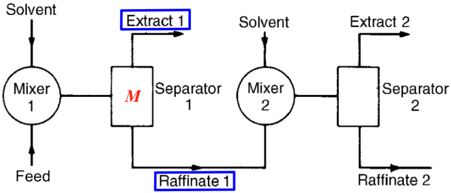
# Link units in *series*




[Richardson and Harker, p 723]

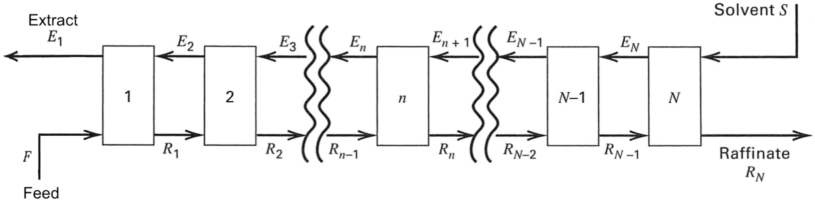
# Q8: send raffinate from Q7 to second mixer-settler




**Question**: how much solvent should we use in the second stage?

# Some theory: *Counter-current* units




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

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

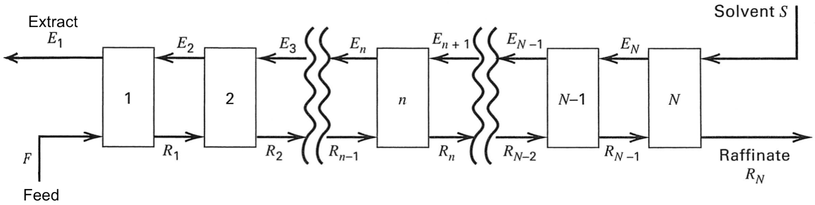
Rearrange:

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

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

Note: each difference is equal to $P$ (look on the diagram where those differences are).

# Counter-current graphical solution




Rearranging again:

$$F + P = E_1$$

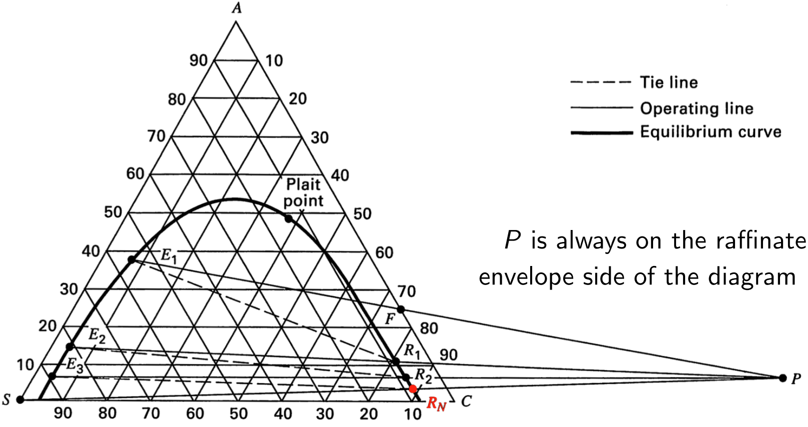
$$R_1 + P = E_2$$

$$R_2 + P = S$$

*Interpretation*: $P$ **is a fictitious operating point**

- $P$ 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 $R_2$ and $S$ in the case of $N = 2$)

# Counter-current graphical solution




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

- 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