Department of Chemical and Environmental Process Engineering

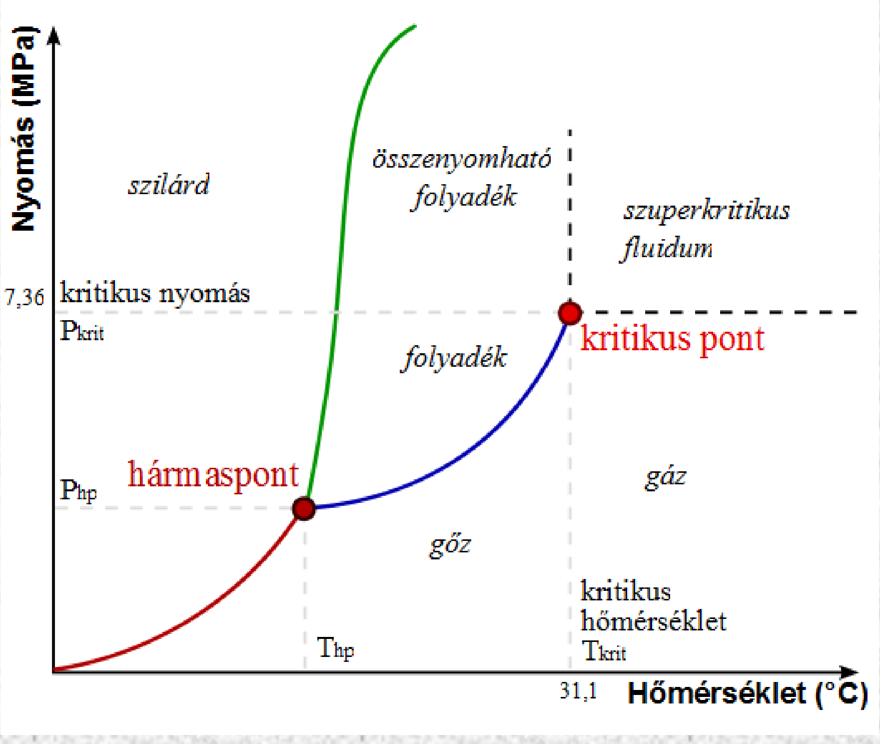
Extraction

Chemical Unit Operations II.

Béla Simándi, Edit Székely

Extraction

I. Liquid-liquid extraction (Solvent extraction)
II. Solid-liquid extraction (Leaching)
III. Supercritical fluid extraction



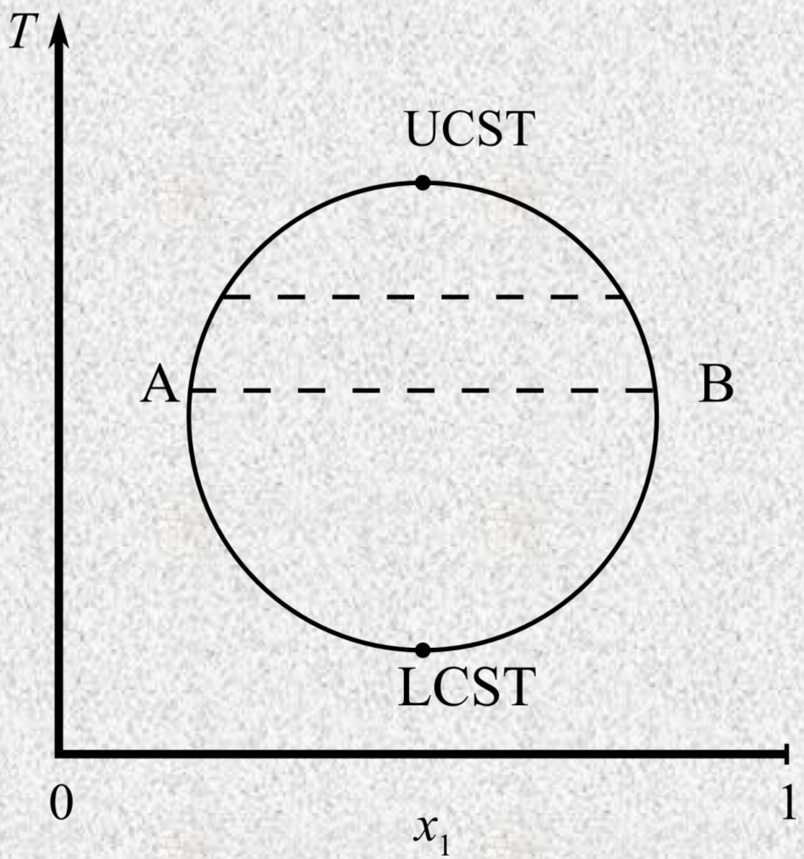
Liquid-liquid extraction
I. Applications

1. Hydrometallurgy
2. Inorganic processes
3. Petroleum industry
4. Pharmaceuticals
5. Waste waters

II. Liquid-liquid equilibrium

Binary systems

P=constant



Curve: composition of saturated solutions of the two components.

Area **enclosed** by the curve: two phase region;
Area **outside** the curve: mixtures that are completely miscible.

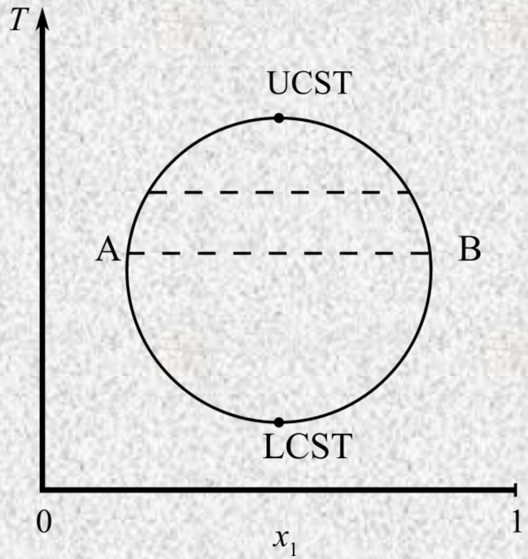
A, B: composition of the phases in equilibrium.

Dashed line: **tie line.**

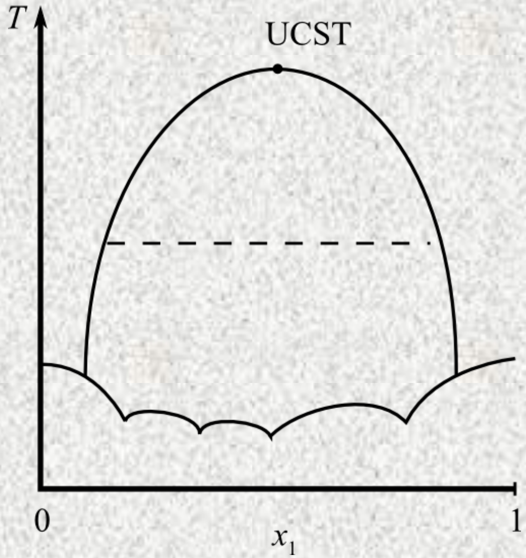
UCST: Upper Critical Solution Temperature.
LCST: Lower Critical Solution Temperature.

Binary systems

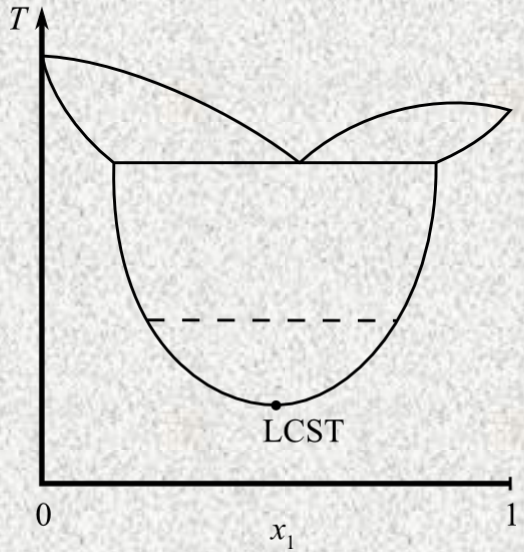
P=constant



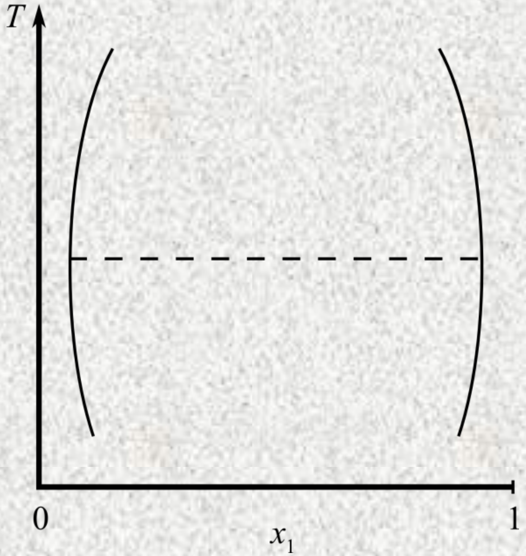
Type I.



Type II.



Type III.

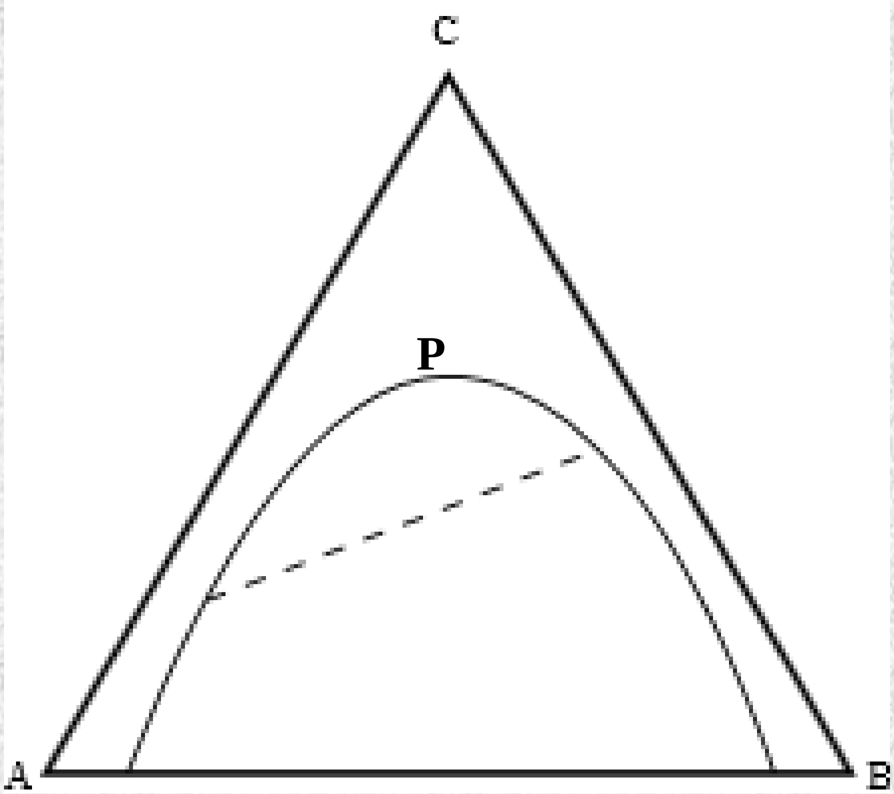


Type IV.

Ternary systems

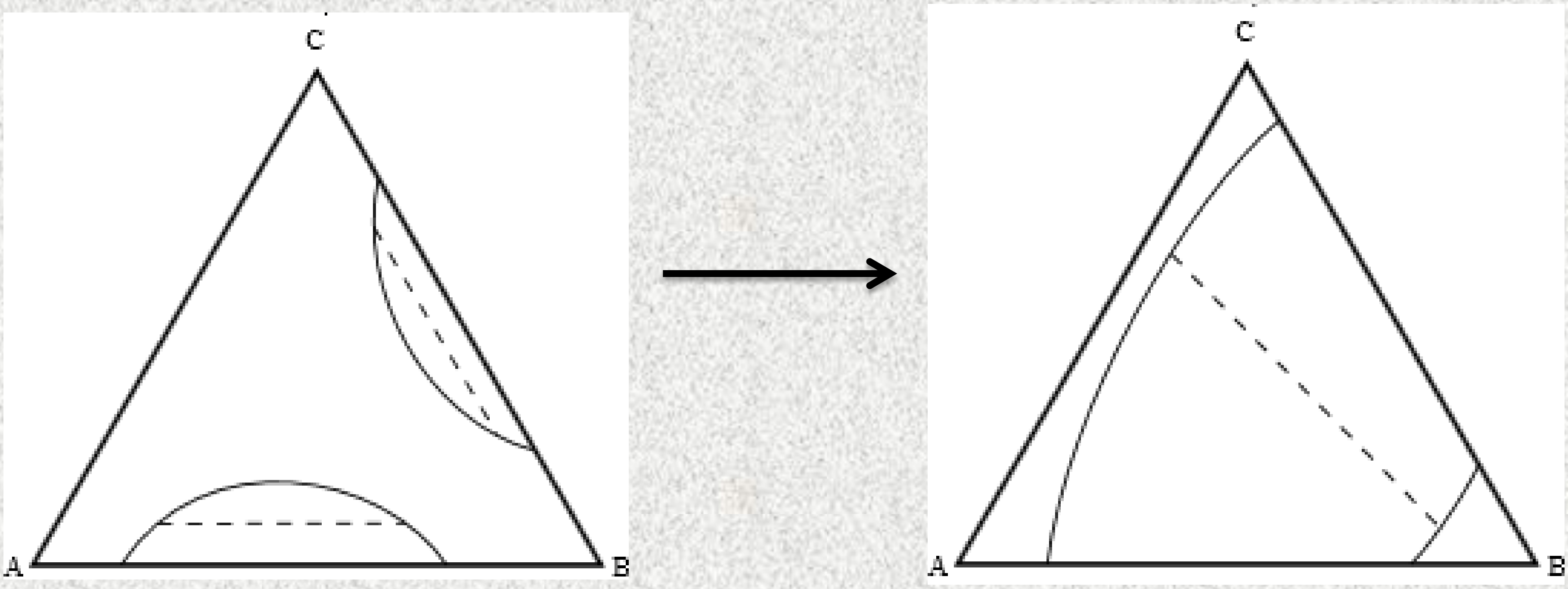
T=constant
P=constant

A, B, C: pure components.
Curve shown within the triangle: the boundary of the two phase region.
Ternary solubility curve=**binodal curve**.
Dashed line = **tie line.**
P: plait point (limit of immiscibility).



Type I.: one partially miscible binary pair.

Ternary systems



Type II.: two partially miscible binary pairs.

III. Single stage extraction (batch extraction)

Theoretically ideal stage: where contact between phases is sufficiently intimate and maintained for a sufficient period of time that equilibrium is established.

Extract phase (E): solvent- rich phase
Raffinate phase (R): solvent-lean phase

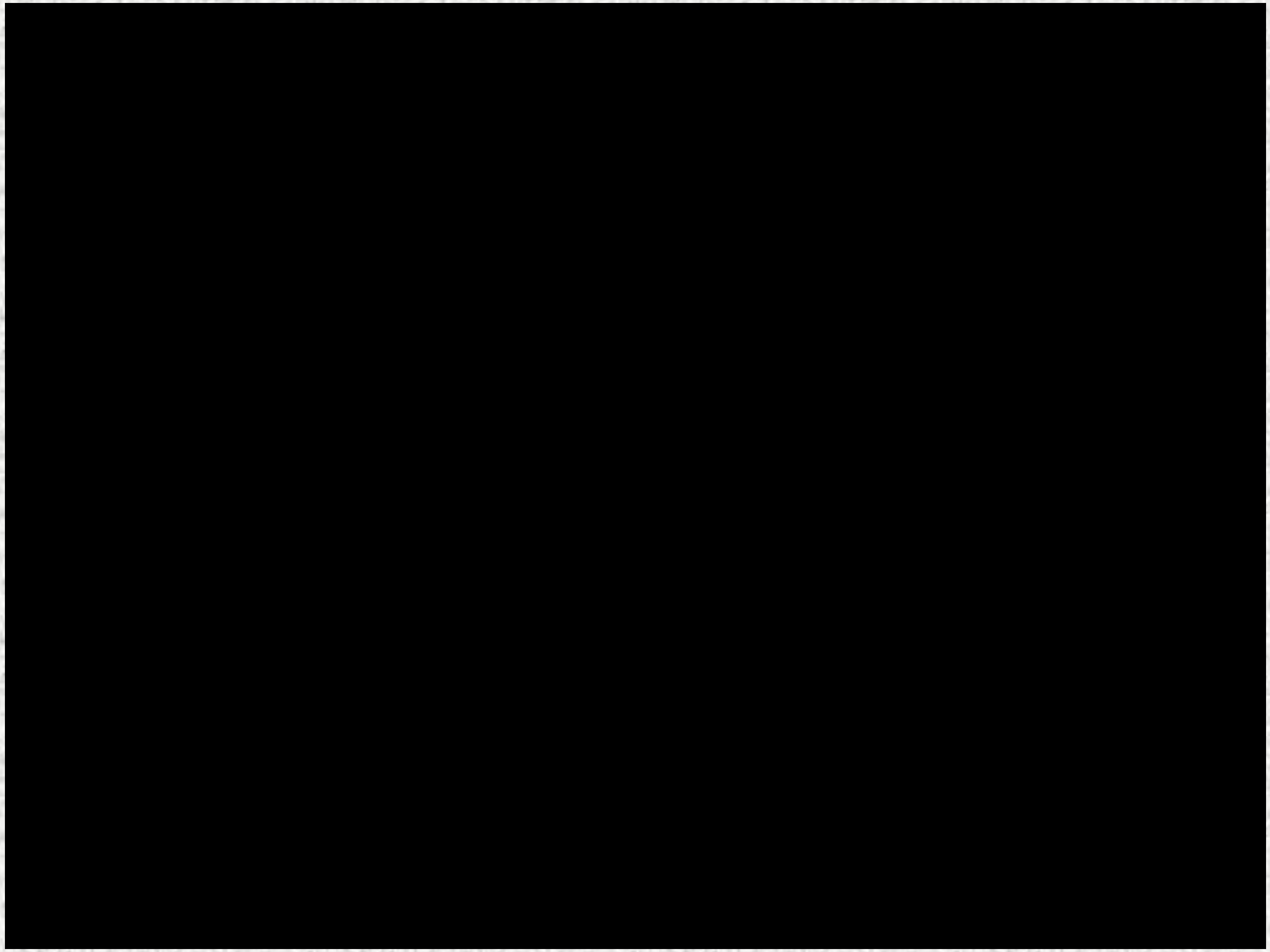
III/1. Simple stirred tank

Equilibrium ratio for a simple ternary system:

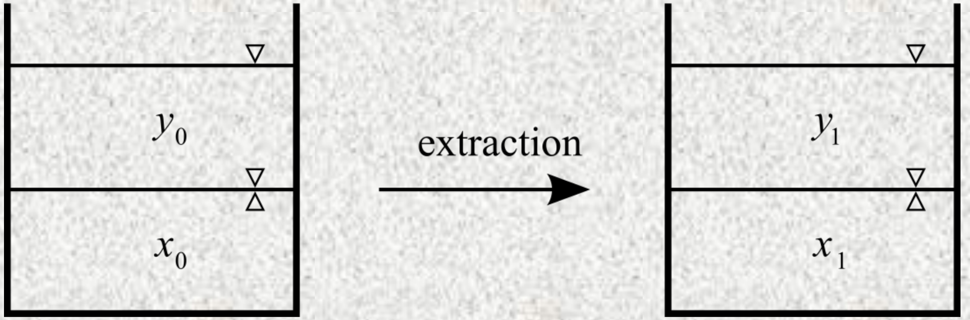
$$m = \frac{y}{x}$$

y: solute concentration in extract phase (wt%)
x: solute concentration in raffinate phase (wt%)
m: equilibrium ratio (distribution coefficient)

http://en.wikipedia.org/wiki/Chemical_reactor



III/1. Simple stirred tank



Total material balance:

$$m_{R_0} + m_{E_0} = m_{R_1} + m_{E_1}$$

Component balance for solute:

$$m_{R_0} * x_0 + m_{E_0} * y_0 = m_{R_1} * x_1 + m_{E_1} * y_1$$

m_{R_0}: mass of the initial solution (kg)
m_{E_0}: mass of the solvent (kg)
m_{R_1}: mass of the raffinate (kg)
m_{E_1}: mass of the extract (kg)
x, y: concentrations (wt%)

III/1. Simple stirred tank

If the solvent and diluent are immiscible and the concentration of solute is low:

$$f = \frac{m_{E_0}}{m_{R_0}} = \frac{m_{E_1}}{m_{R_1}} = constant$$

$$y_1 = m * x_1 \quad \longrightarrow \quad x_0 + f * y_0 = x_1 + f * y_1 = x_1 + f * m * x_1$$

$$\boxed{E = \frac{m_{E_1} * y_1}{m_{R_1} * x_1} = f * m}$$

Extraction factor

$$x_0 + f * y_0 = x_1 * (1 + E)$$

$$x_1 = \frac{x_0}{1+E} + \frac{E * (\frac{y_0}{m})}{1+E}$$

If y_0=0 (neat solvent) $\quad \left\{ x_1 = \frac{x_0}{1+E} \right.$

III/2. Multiple-extraction

The raffinate from the first stage is extracted with fresh solvent of the same composition in successive stages.

General solution (if neat solvent is used):

First stage
$$x_1 = x_0 * \frac{1}{1+E}$$

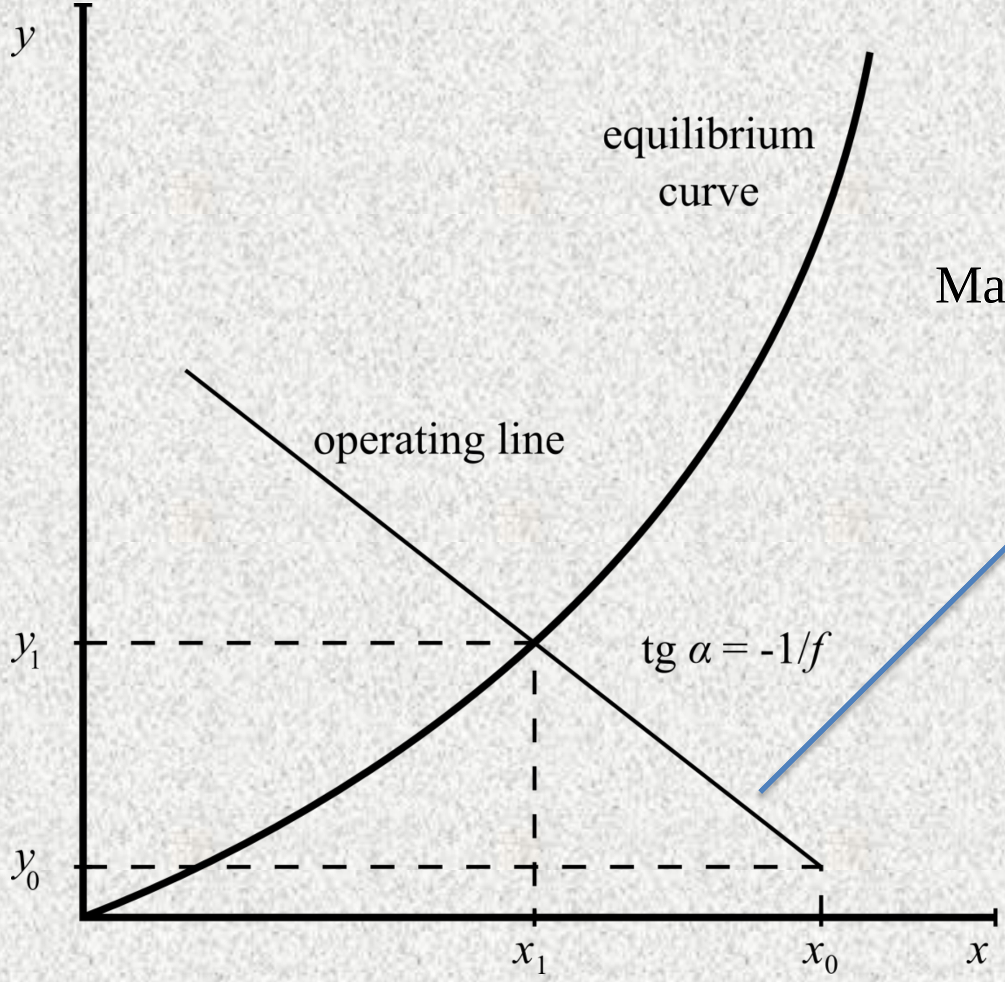
Second stage
$$x_2 = x_1 * \frac{1}{1+E} = x_0 * \frac{1}{(1+E)^2}$$

Third stage
$$x_3 = x_2 * \frac{1}{1+E} = x_0 * \frac{1}{(1+E)^3}$$

n^{th} stage
$$x_n = x_0 * \frac{1}{(1+E)^n}$$

III/2. Multiple-extraction

If liquids are completely immisible or at least their solubility does not change over the range of concentration of distributed substance:

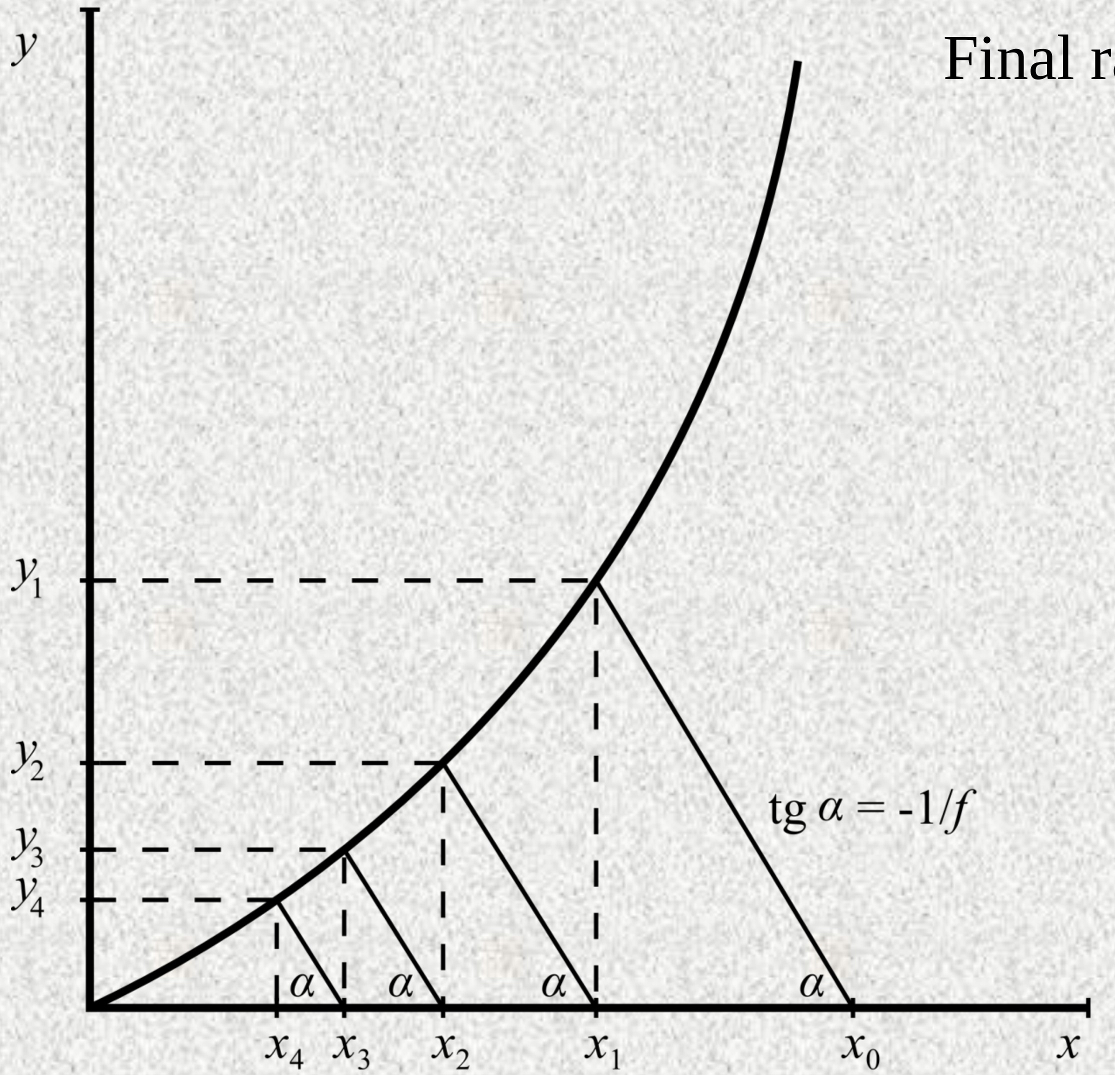


Material balance equation gives:

$$y_1 = \frac{1}{f} * (x_0 - x_1) + y_0$$

$$tg\alpha = -\frac{1}{f}\text{; through } (x_0, y_0)$$

III/2. Multiple-extraction



Final raffinate concentration.

$$y_1 = \frac{1}{f} * (x_0 - x_1) + y_0$$

III/2. Multiple-extraction
Triangular diagram

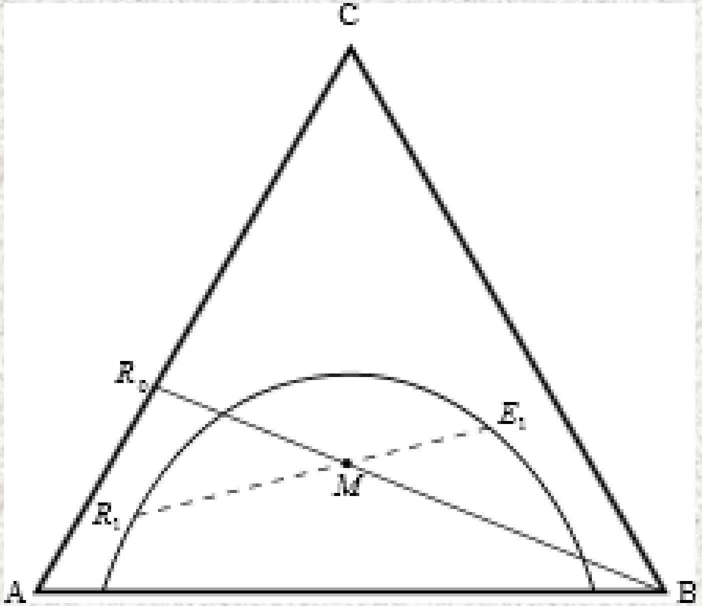
- If ´f´ and ´m´ depend on the composition.

Material balance:

$$m_{R_0} + m_{E_0} = m_{R_1} + m_{E_1}$$

$$m_{R_0} * x_0 + m_{E_0} * y_0 = m_{R_1} * x_1 + m_{E_1} * y_1$$

x_{M1} : overall composition of the ternary mixture, **M1** point can be located by the lever-arm rule.



Calculation:

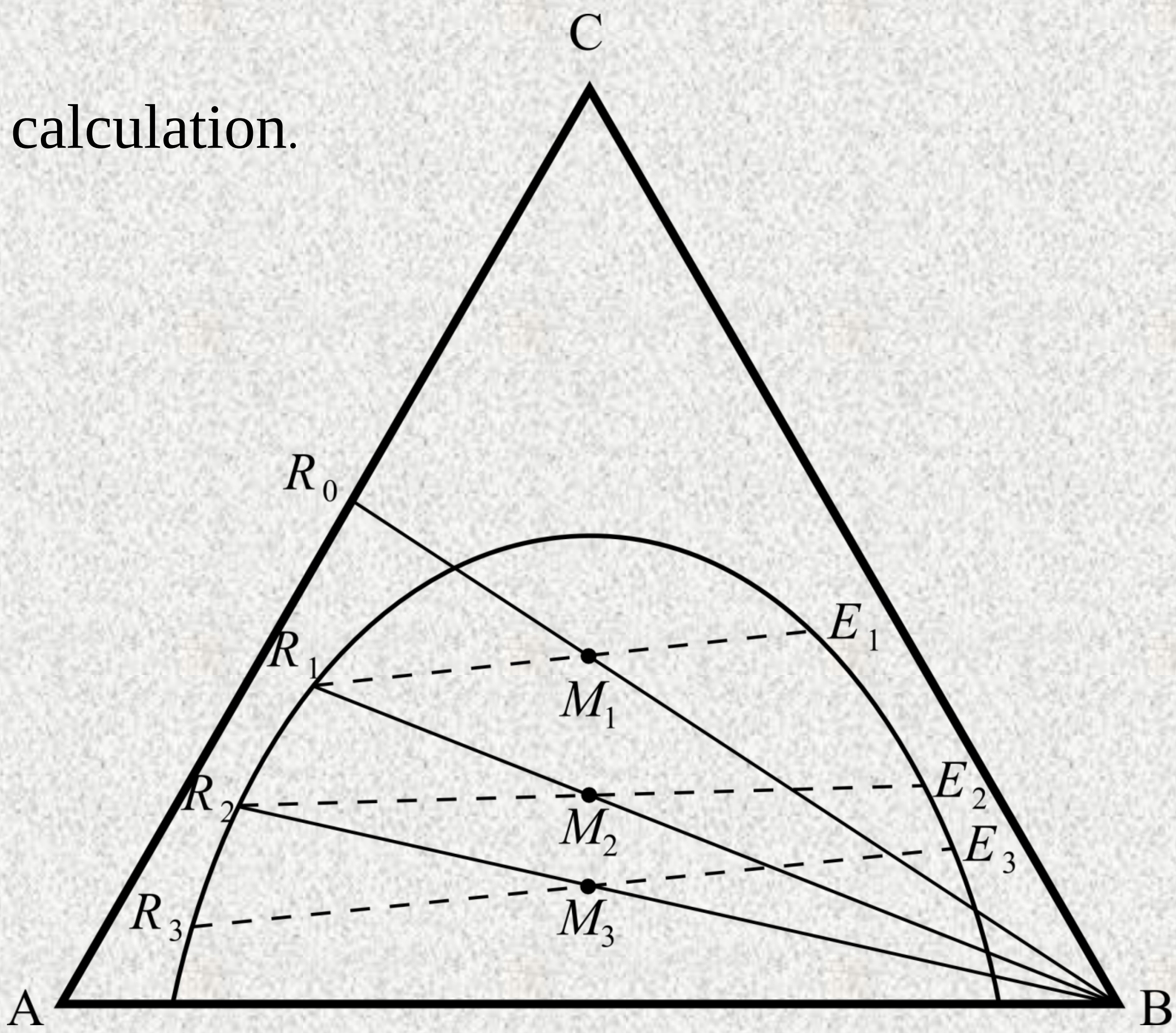
$$x_{M_1} = \frac{m_{R_0} * x_0 + m_{E_0} * y_0}{m_{R_0} + m_{E_0}}$$

$$x_{M_1} = \frac{m_{R_1} * x_1 + m_{E_1} * y_1}{m_{R_1} + m_{E_1}}$$

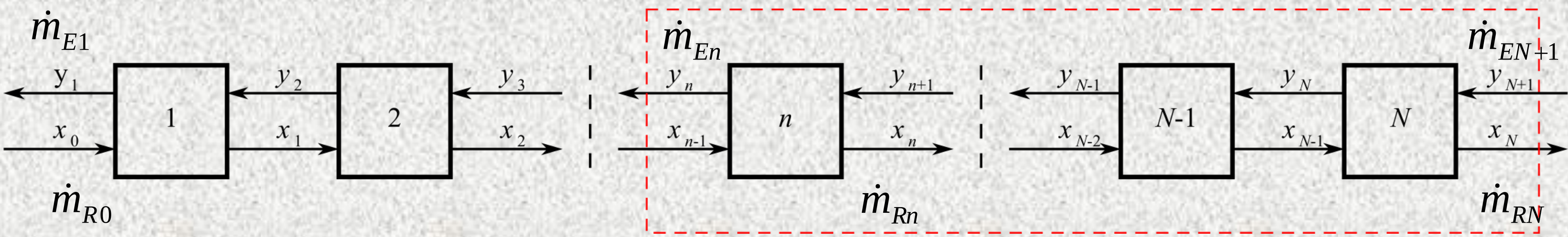
III/2. Multiple-extraction

Triangular diagram

Methods of calculation.



III/3. Continuous extraction



$\dot{m}_{En}$: extract mass flowrate leaving stage n (kg/s)

y_n: solute concentration in $\dot{m}_{E_n}$ (mass fraction)

$\dot{m}_{Rn}$: raffinate flowrate leaving stage n (kg/s)

x_n: solute concentration in $\dot{m}_{R_n}$ (mass fraction)

N: number of equilibrium stages (-)

III/3. Continuous extraction

- If the solvent and diluent are completely immiscible and m is constant:

$$\frac{x_N - \frac{y_{N+1}}{m}}{x_0 - \frac{y_{N+1}}{m}} = \frac{E-1}{E^{N+1}-1}$$

$$E = f * m \qquad \textit{extraction fraction}$$

$$f = \frac{\dot{m}_E}{\dot{m}_R} \qquad \textit{flowrate ratio}$$

If E=1 $\longrightarrow$ $$\frac{x_N - \frac{y_{N+1}}{m}}{x_0 - \frac{y_{N+1}}{m}} = \frac{1}{N+1}$$ Kremser (1930)

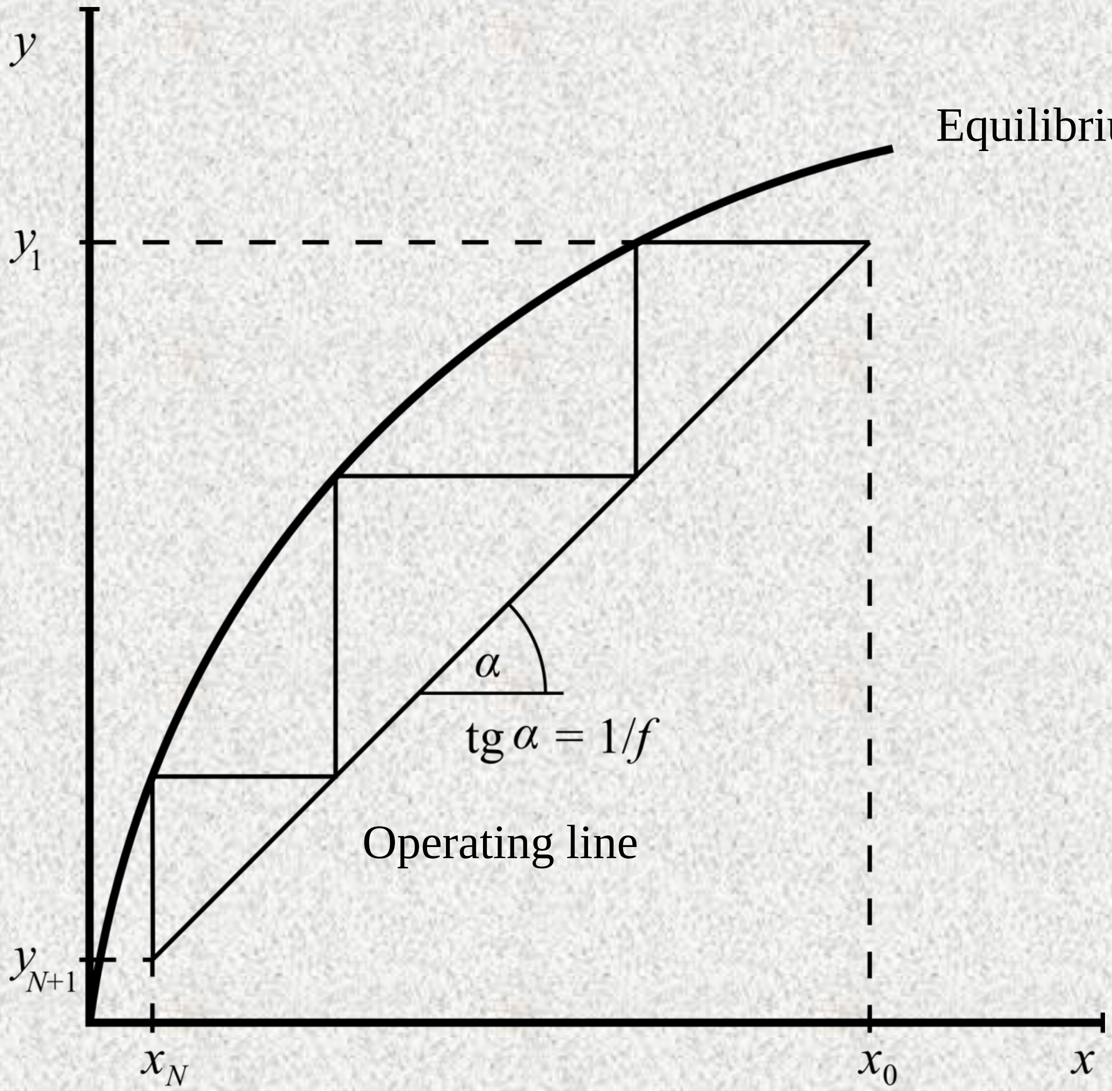
- If the solvent and diluent are completely immiscible or at least their solubility does not change over the range of concentration of distributed substance: **McCabe-Thiele analysis**.

$$\dot{m}_R * x_{n-1} + \dot{m}_E * y_{N+1} = \dot{m}_R * x_N + \dot{m}_E * y_n \longrightarrow \boxed{y_n = \frac{1}{f} * (x_{n-1} - x_N) + y_{N+1}}$$

Operating line

Raffinate and extraction rates are constant.

III/3. Continuous extraction

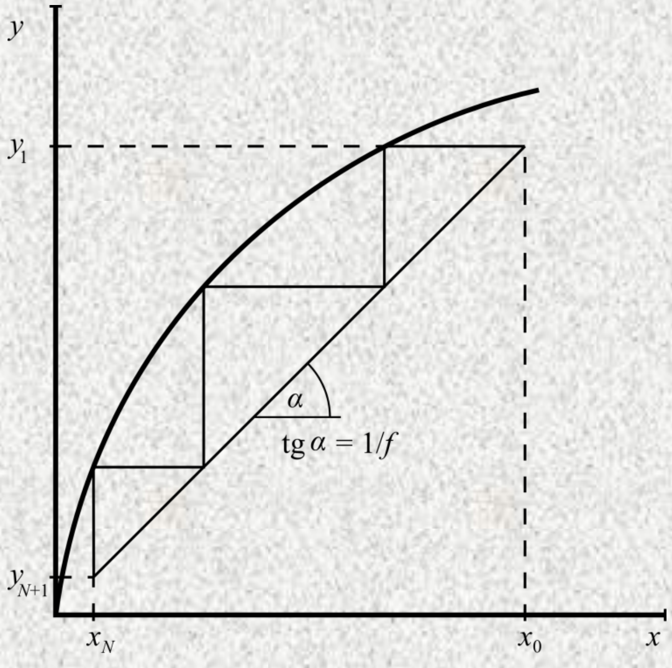


$$y_n = \frac{1}{f} * (x_{n-1} - x_N) + y_{N+1}$$

tgα=1/f; through (x_N, y_{N+1})

III/3. Continuous extraction

- If ´f´ changes only because of transfer of solute from raffinate phase to the extract phase the same diagram and method can be used.



$$y = \frac{solute}{solute - free\ solvent}$$

$$x = \frac{solute}{solute - free\ diluent}$$

New coordinate system.

Total flow rates:

$\dot{m}_E$: solute-free extract (usually neat solvent)

$\dot{m}_R$: solute-free raffinate (usually neat diluent)

- Triangular diagrams can be used for partially miscible systems!
- System of more than three components require computers for solution of their model equations.

IV. Selection of solvent in extraction

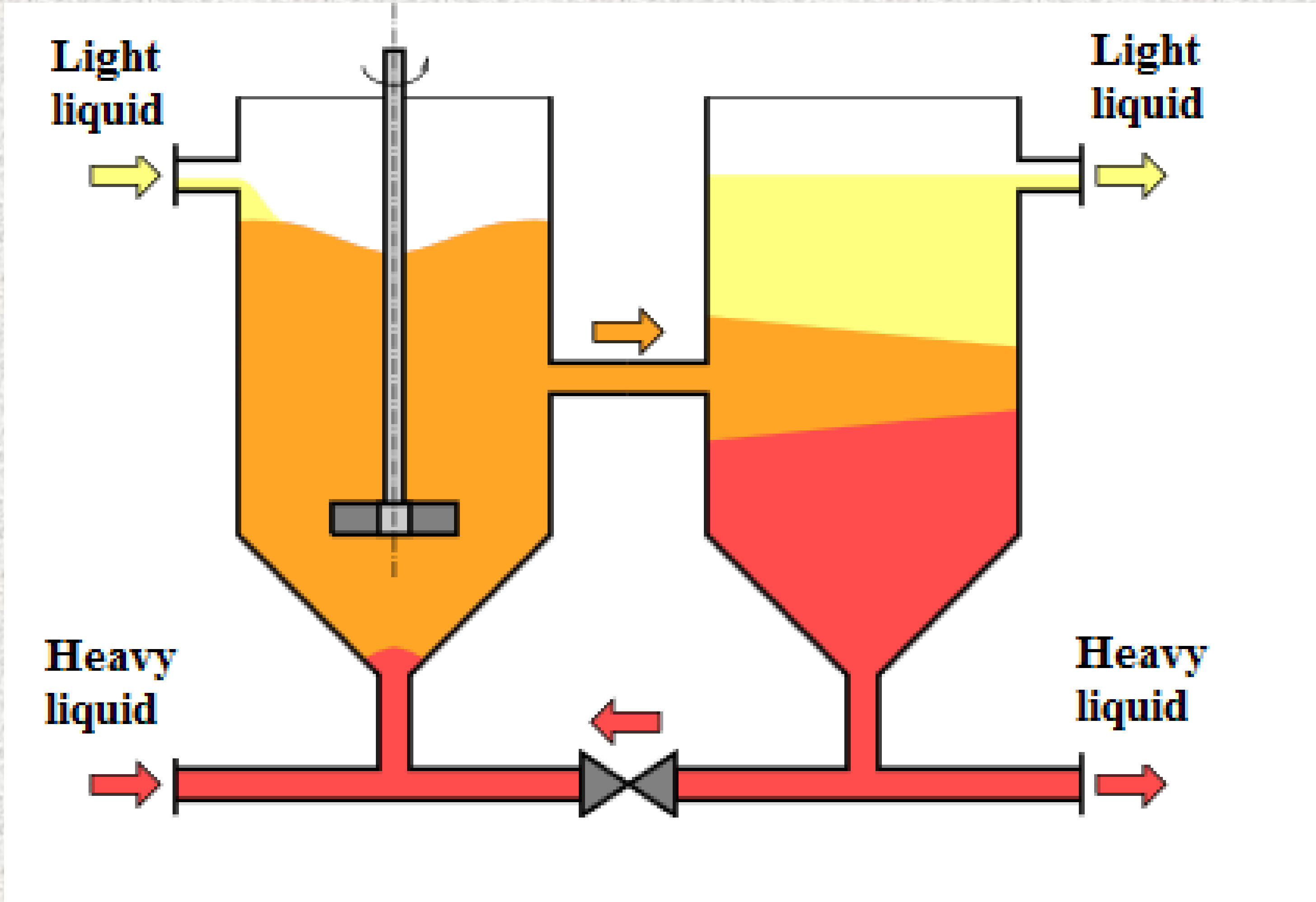
The proposed solvent must form a separate phase from the feed solution and should be able to extract the solute from the feed solution.

1. Distribution coefficient (m)
2. Solubility
3. Density ($\Delta\rho$>150 kg/m^3)
4. Interfacial tension
5. Viscosity
6. Chemical reactivity and stability
7. Vapour pressure
8. Flammability
9. Toxicity
10. Cost analysis

V. Equipment

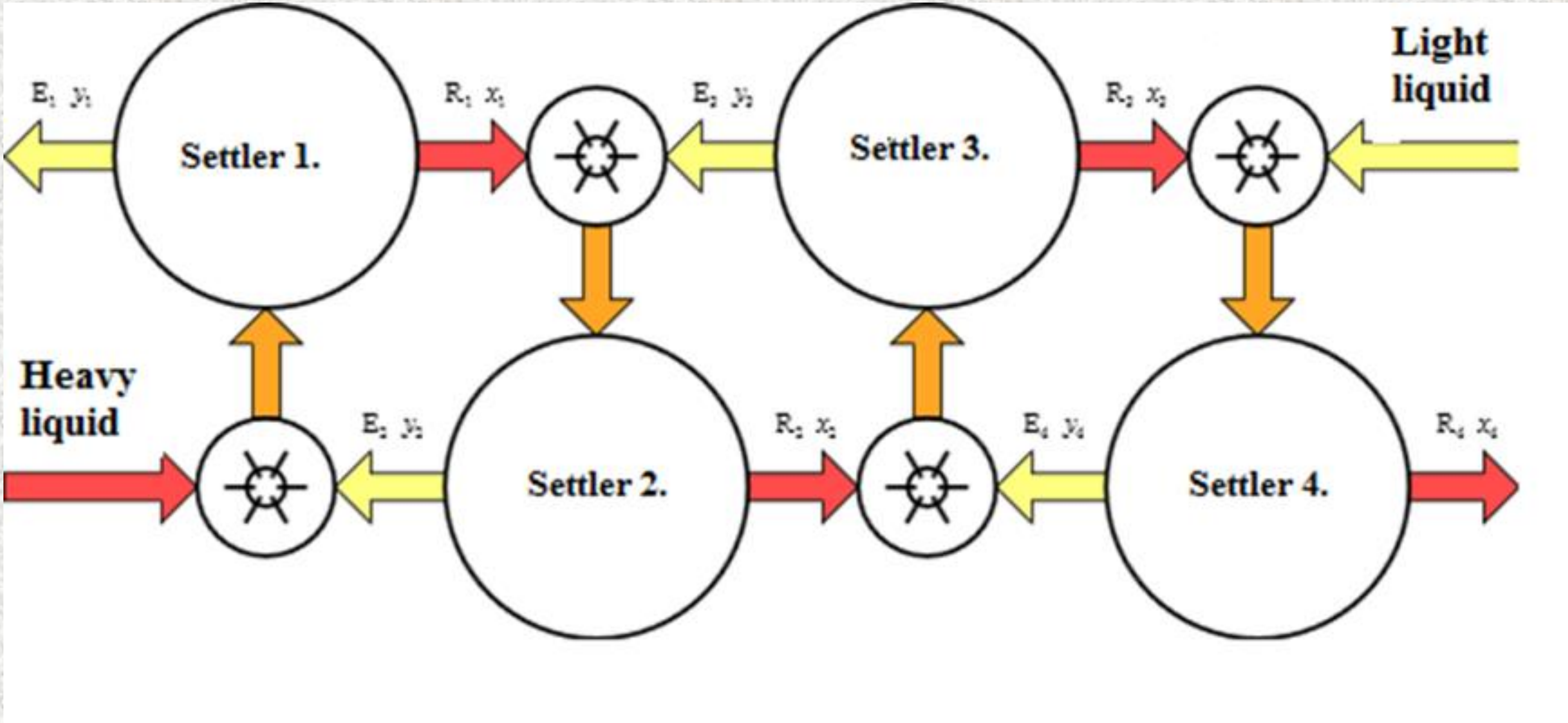
1. Mixer-settler or a series of mixer-settlers
2. A column, which may be agitated or pulsed
3. Some other contactor such as a centrifugal device

V/1. Mixer-settler



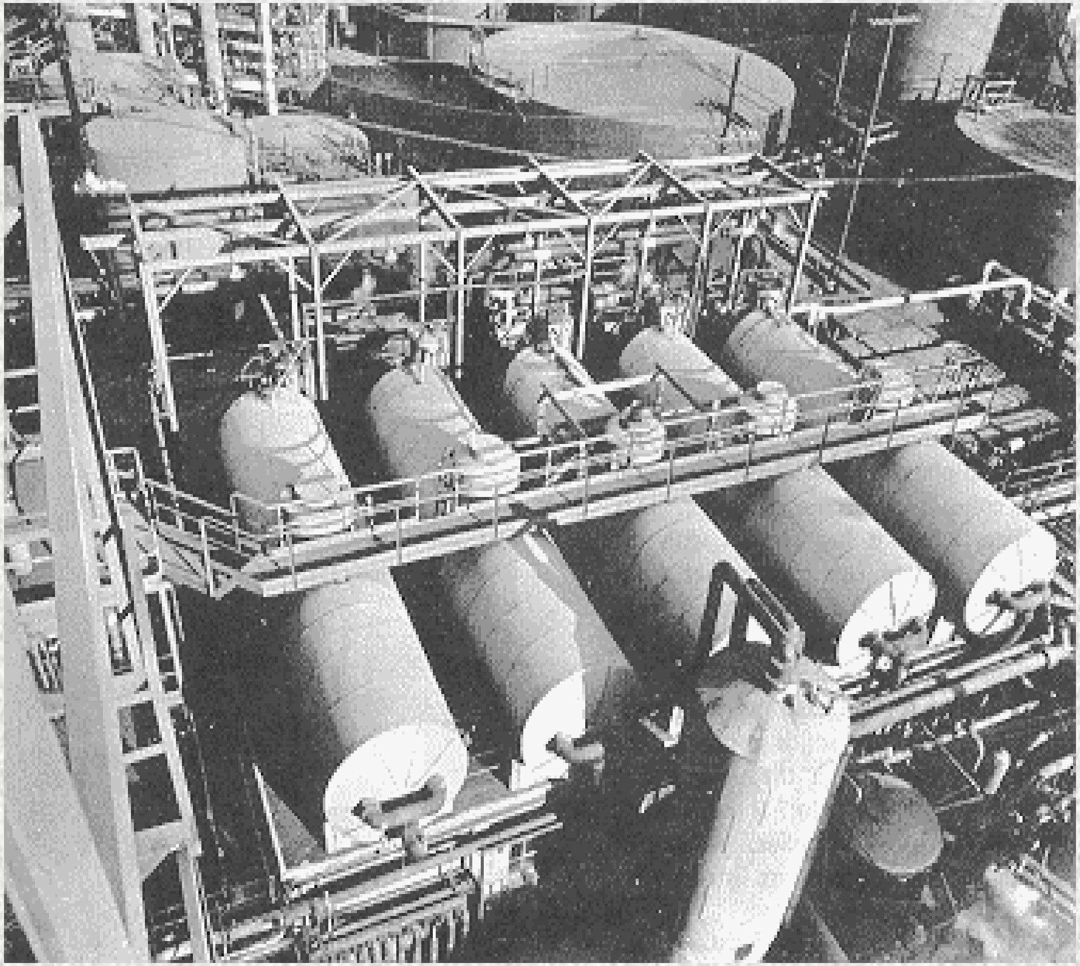
The separating efficiency is proportional to the area of the phase interface.

V/1. Mixer-settler cascade

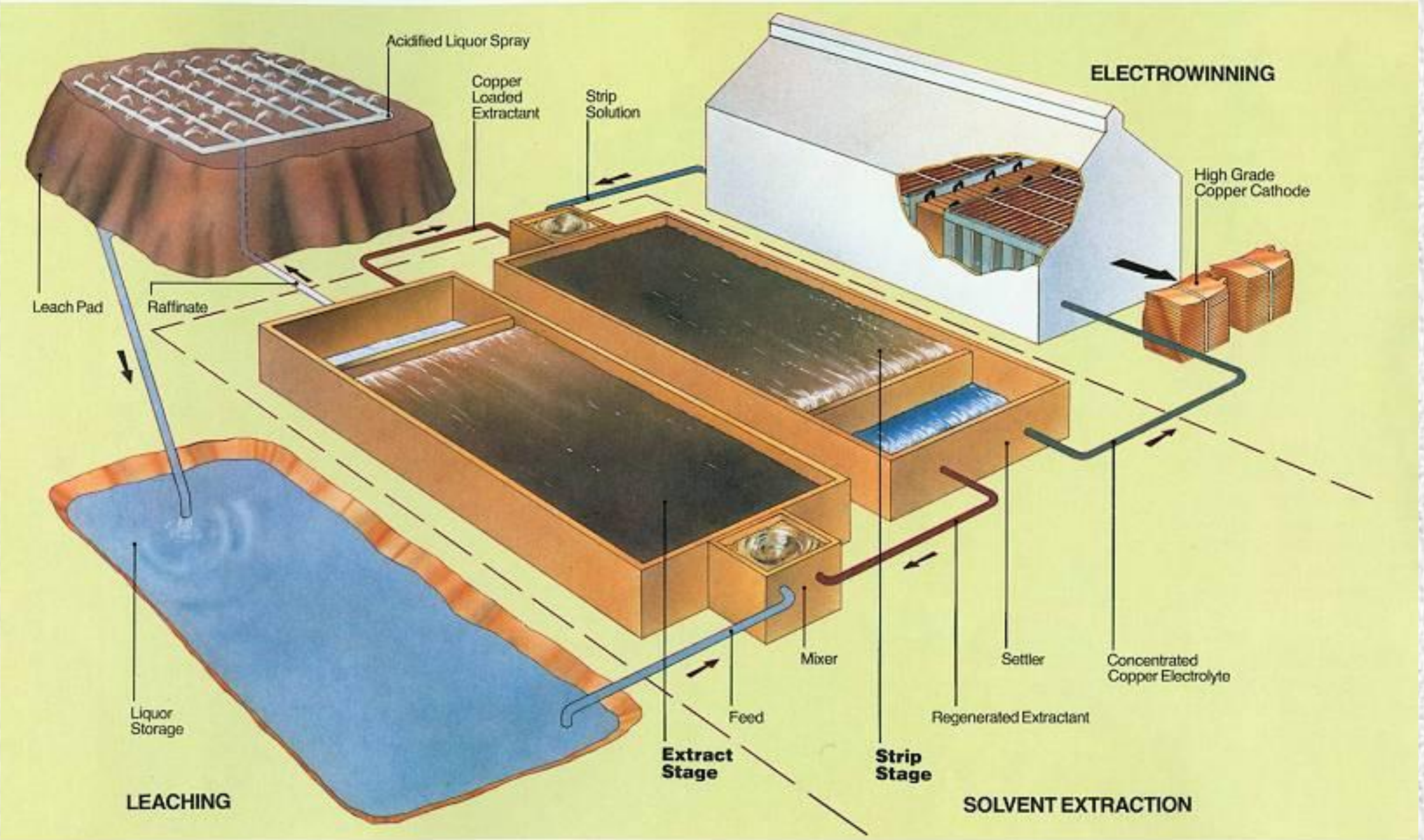


Large hold up volumes, long residence time, large physical size.

V/1. Mixer-settler cluster



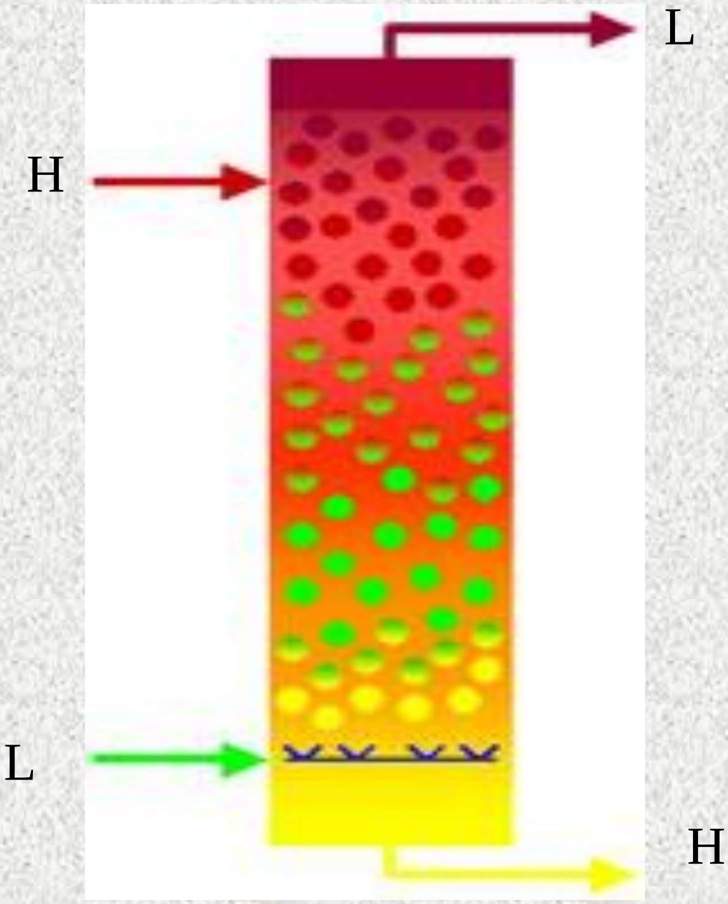
V/1. Copper's extraction in Mixer-settler



V/2. Columns without energy input

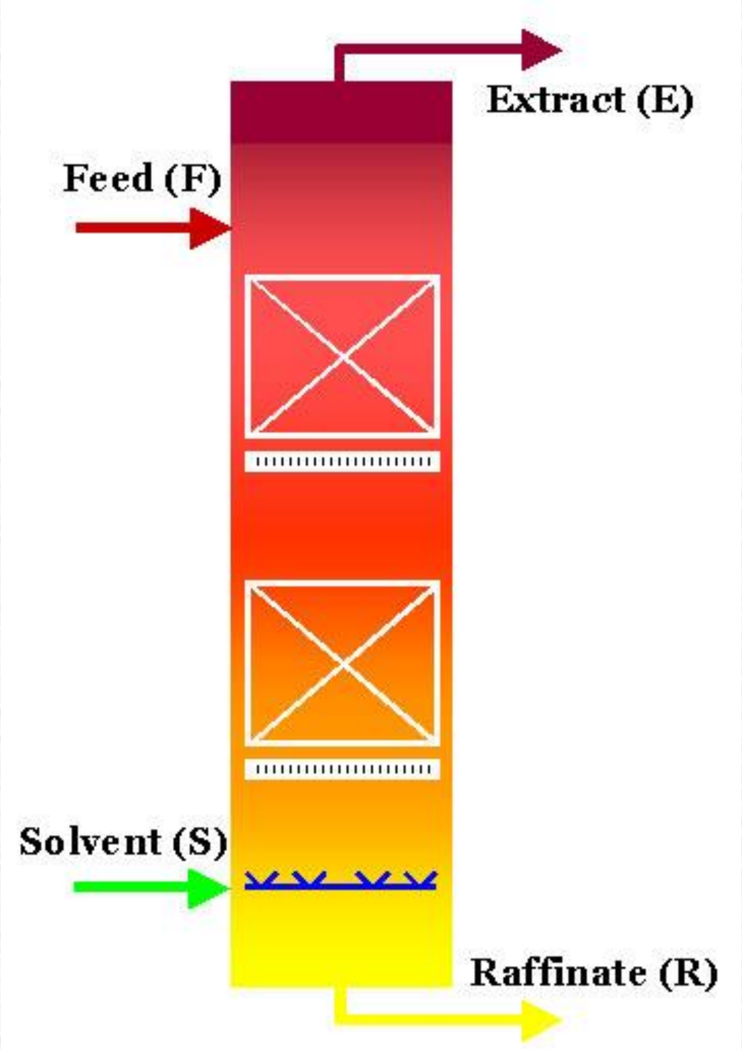
a.) Spray column

Simplicity
High throughput
Low cost



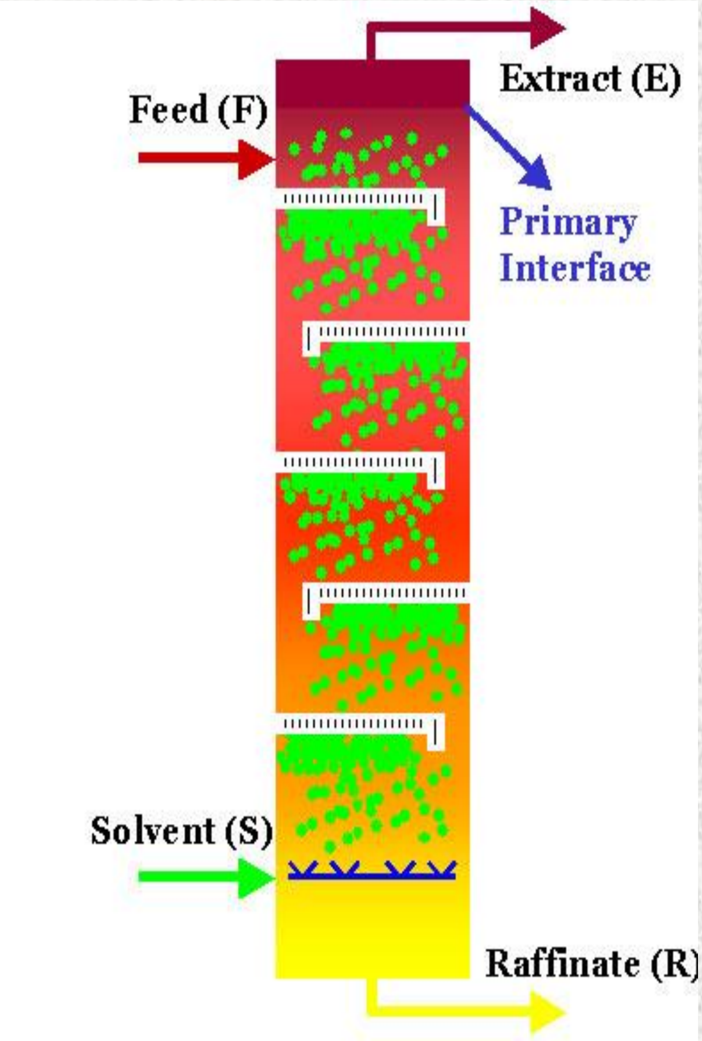
Application: little in industry.

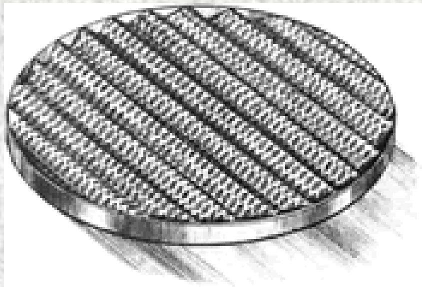
b.) Packet columns



- The most purposes random packing;
- The packing should be wetted by the continuous phase.

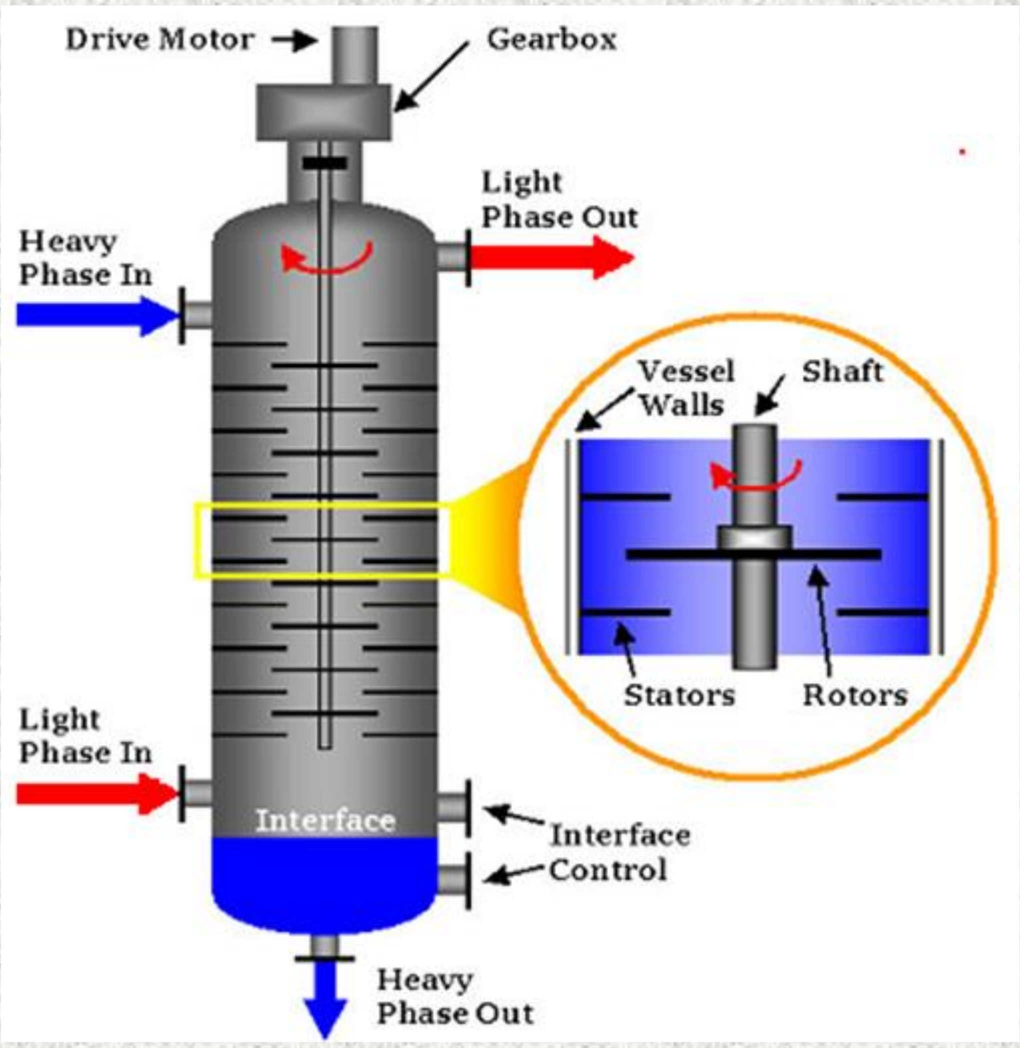
c.) Sieve-Trey column

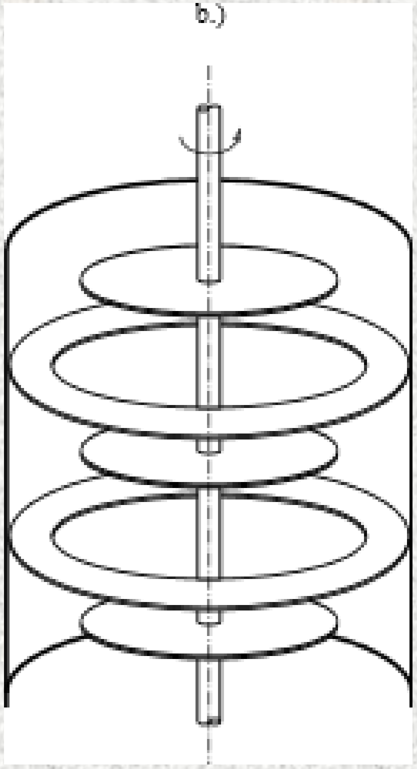




Application: in petroleum industry.

V/3. Columns with energy input
a.) Rotating Disc Contactor (RDC)

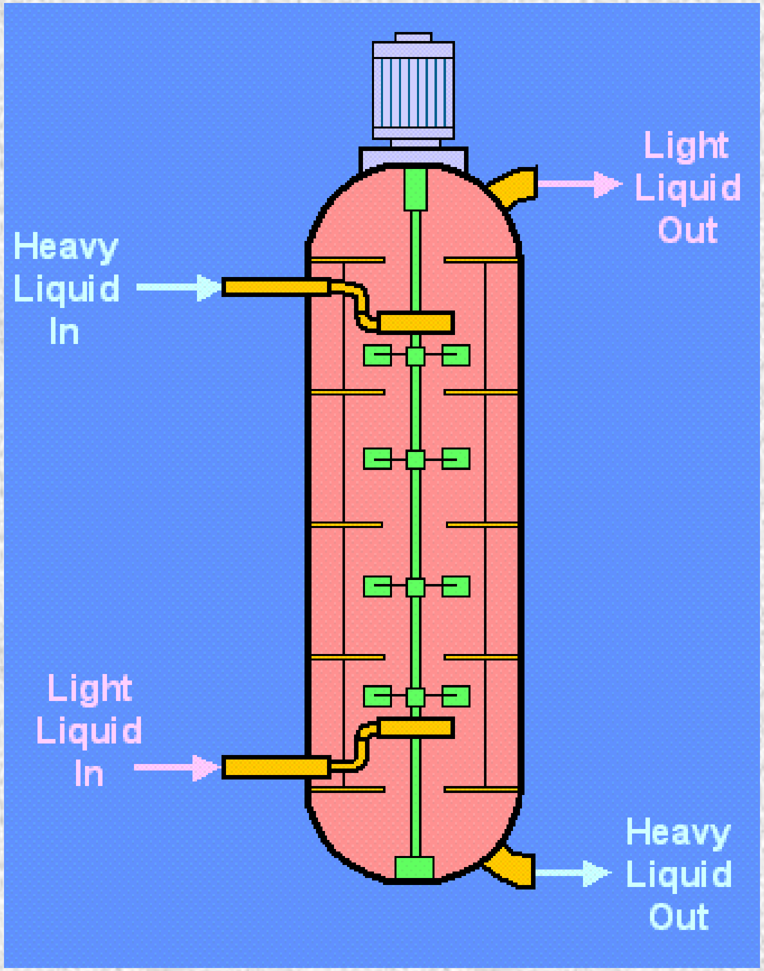


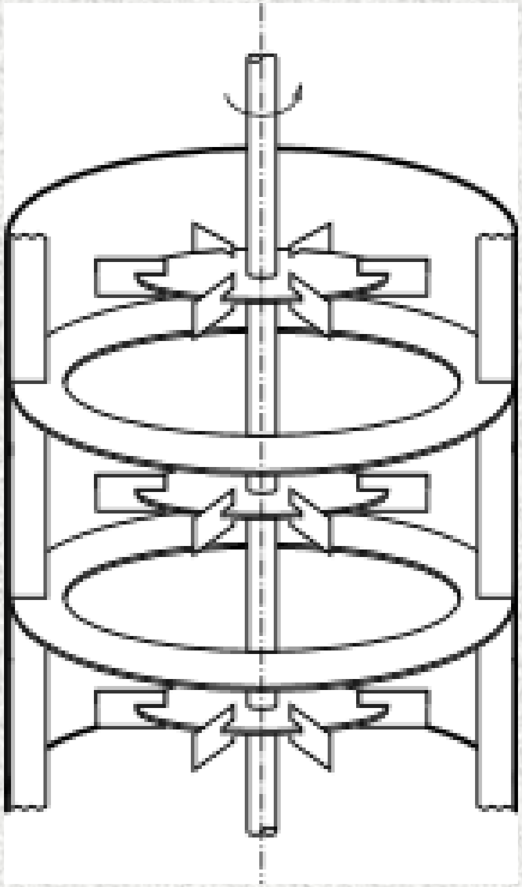


Shell
1948

Application: in petroleum and chemical industries, waste water treatment.

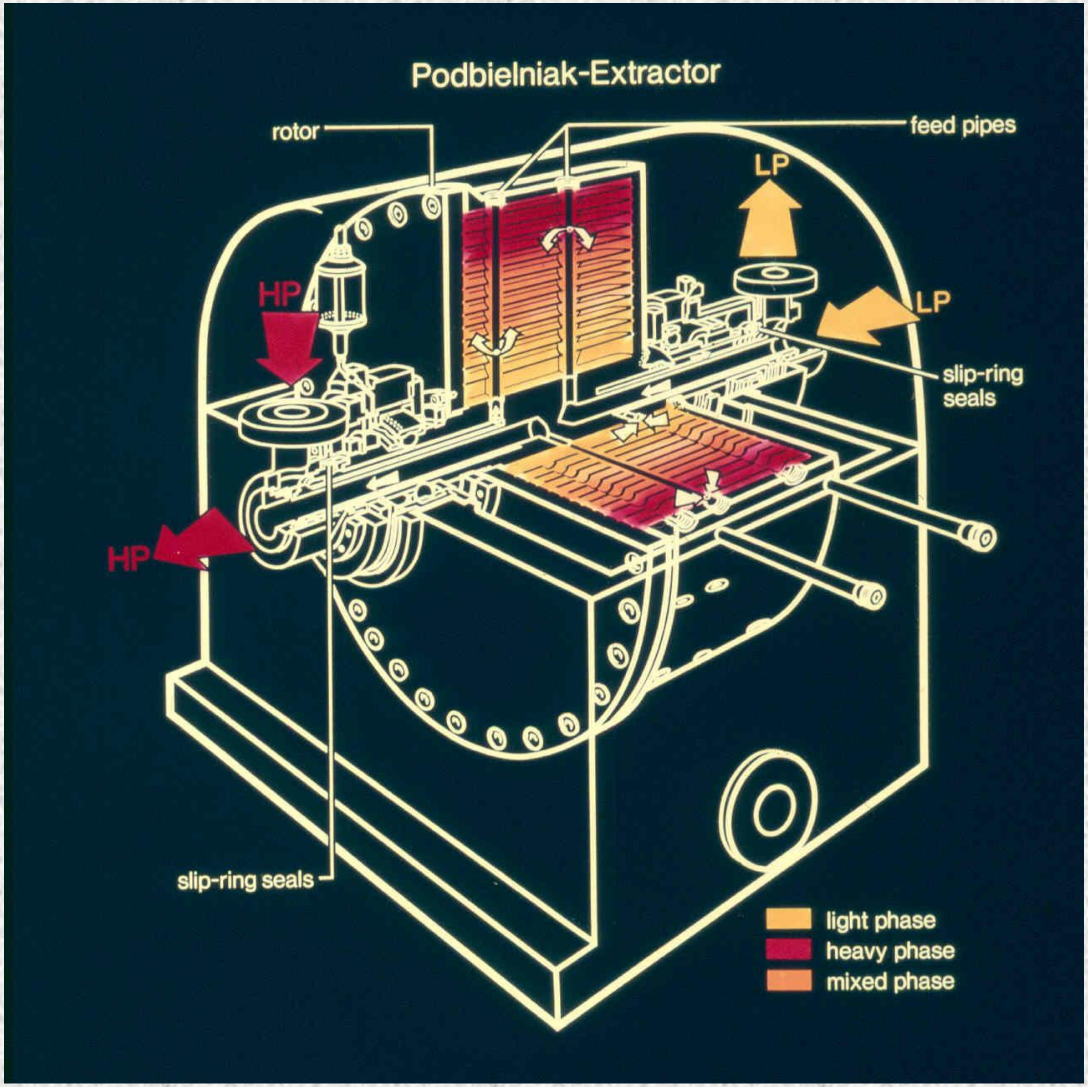
b.) Oldshue-Rushton column (1952, USA)





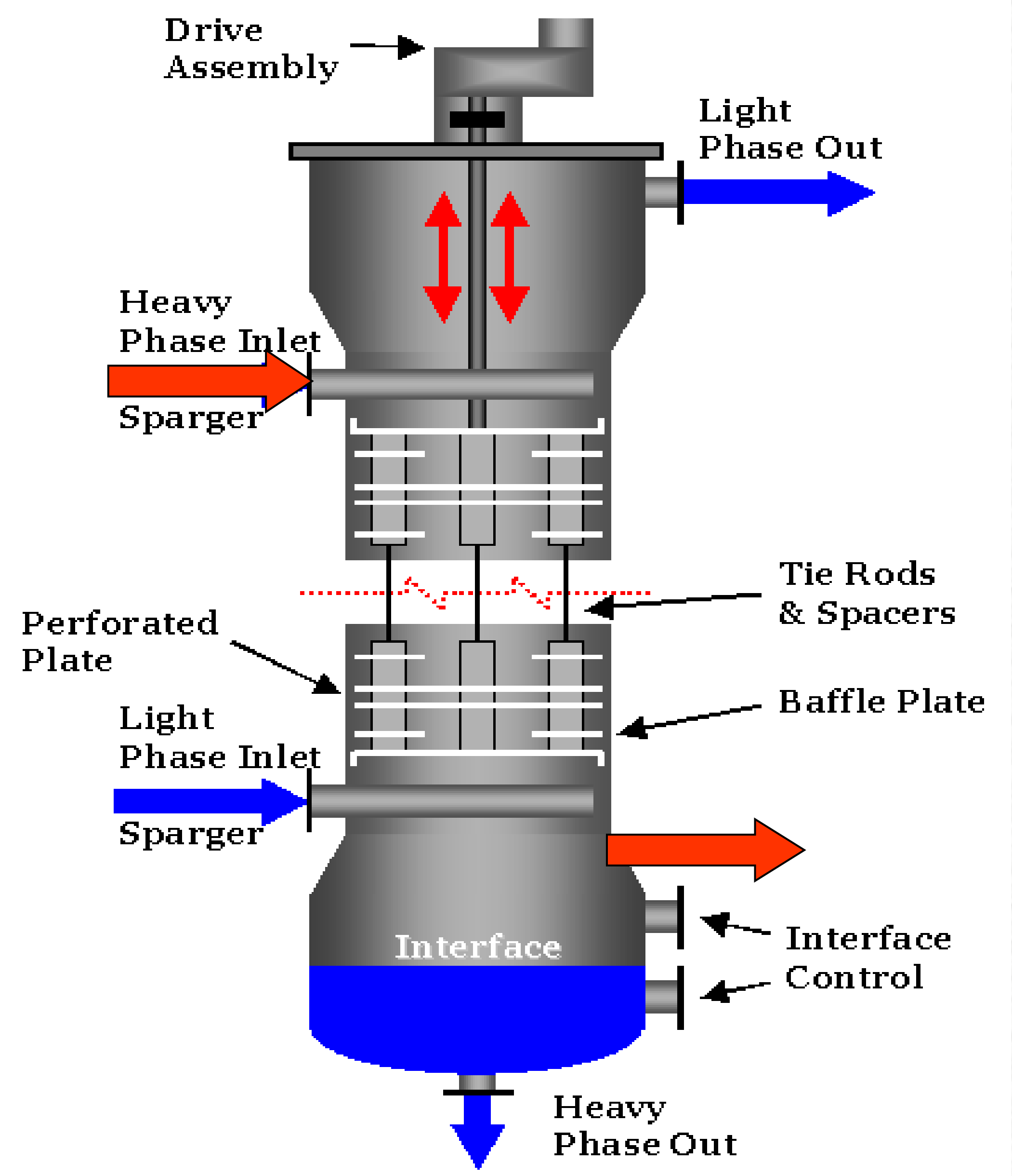
http://www.separationprocesses.com/Extraction/SE_Chp03c.htm

Centrifugal Extractor (Podbielniak-Extractor)



Centrifugal extractor (Podbielniak-Extractor)

Karr column



Drive
Assembly
Light
Phase Out
Heavy
Phase Inlet
Sparger
Tie Rods
& Spacers
Perforated
Plate
Baffle Plate
Light
Phase Inlet
Sparger
Interface
Interface
Control
Heavy
Phase Out

Karr column

KMPS
Extraction Technology Group
www.modular-process.com

Thank you for your attention!