

Solvent Extraction

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Agenda

- ◆ Fundamentals of Solvent Extraction
- ◆ LLE and VLLE in binary systems
- ◆ Representing a three-component system
- ◆ Liquid-Liquid Equilibria in ternary systems
- ◆ Iso-activity condition
- ◆ LLE in a ternary diagram
- ◆ Material balances
- ◆ Single ideal stage process
- ◆ Multiple countercurrent stages in series
- ◆ Extraction column
- ◆ Extraction equipment's
- ◆ Extraction with Aspen+: Extrac

Solvent Extraction fundamentals

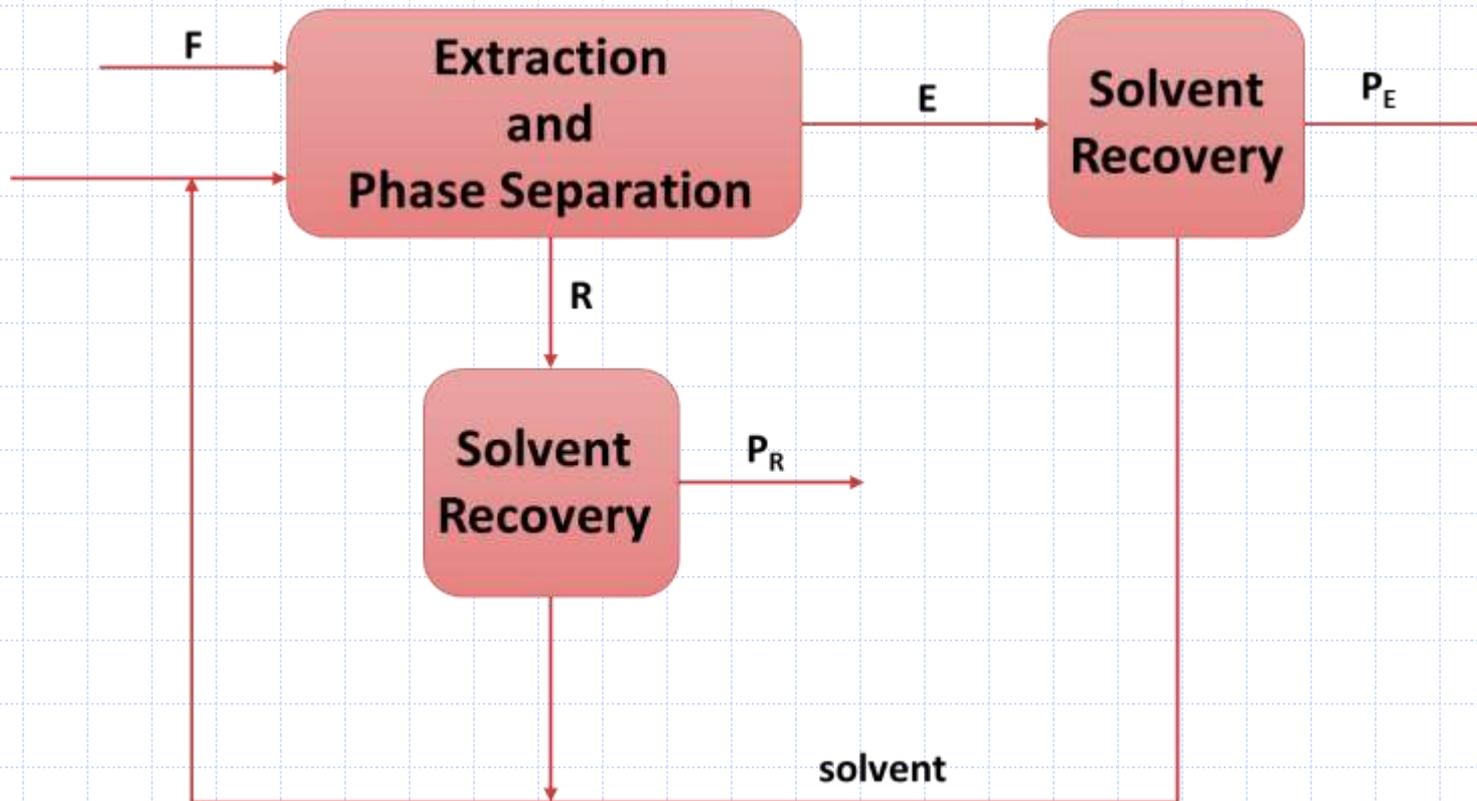
- ◆ The separation of components from a liquid mixture can be achieved also by solvent extraction. Fractionation by **solvent extraction** is a unit operation to separate one or more components from a liquid (or a solid) phase mixture by **selectively dissolve it into a solvent**.
- ◆ In the case the feed mixture is a liquid, it is also called liquid-liquid extraction. **The second phase** needed to achieve separation is a suitable liquid.
- ◆ This separation operation is possible thanks to the different affinity (i.e. **activity coefficients**) of components in a given solvent.
- ◆ The solvent is chosen so that to maximize its affinity with respect to one (or more) components of the starting liquid (or solid) mixture to be separated from the rest of the liquid (solid) components.

Solvent Extraction fundamentals

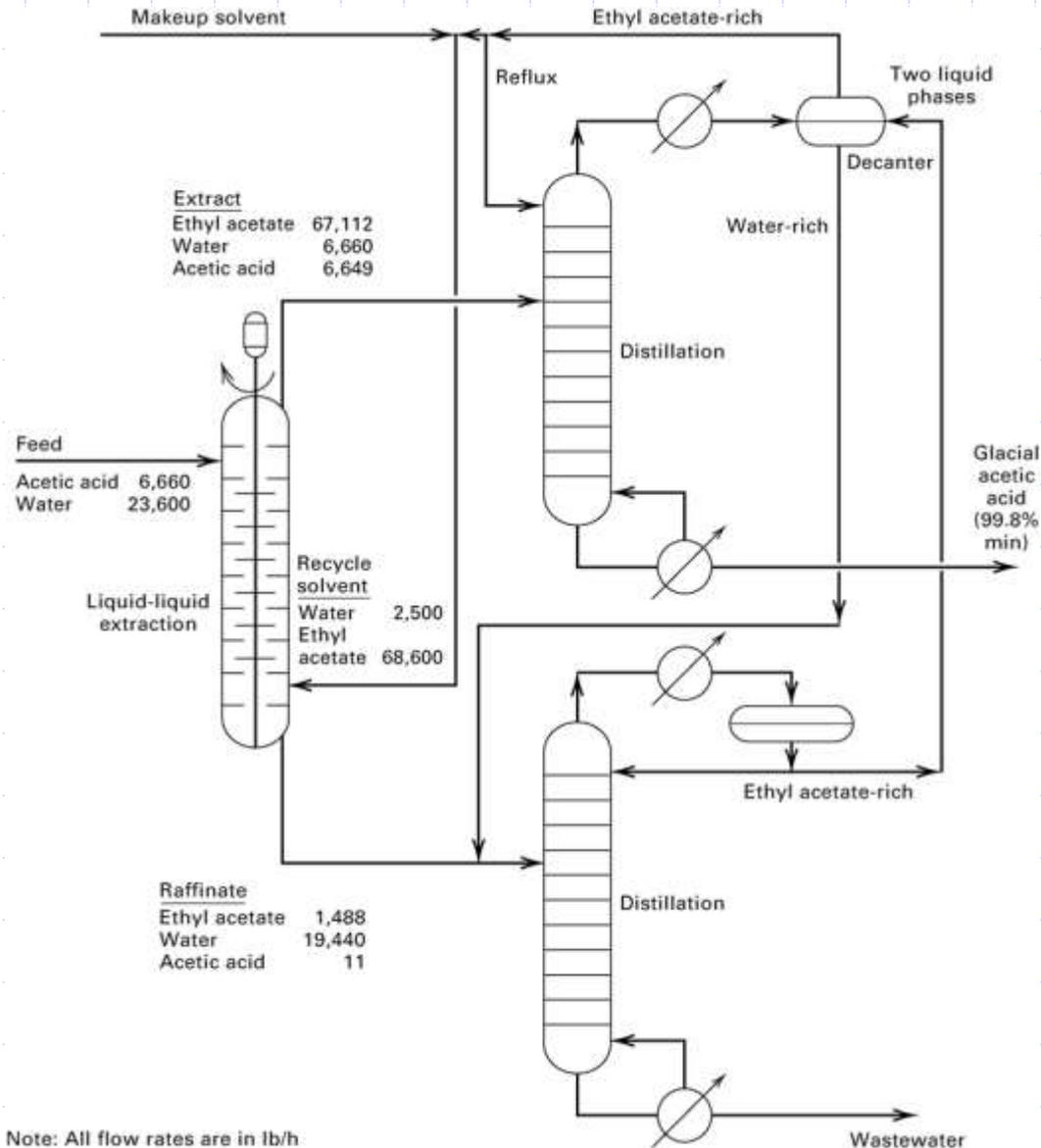
- ◆ The solvent is selected to obtain a favorable distribution of the components of interest between the two phases.
- ◆ Solvent extraction can be carried out both in a discontinuous or continuous single-stage, and in a continuous multistage mode.
 - It has been an operation in the chemical industry for a long time, although not as widely used as distillation.
- ◆ Solvent extraction is a **non-thermal separation process**.

Solvent Extraction reference diagram

- ◆ **Extract** and a **Raffinate**. The solvent is recovered and recycled together with a make-up



Typical liquid-liquid extraction process



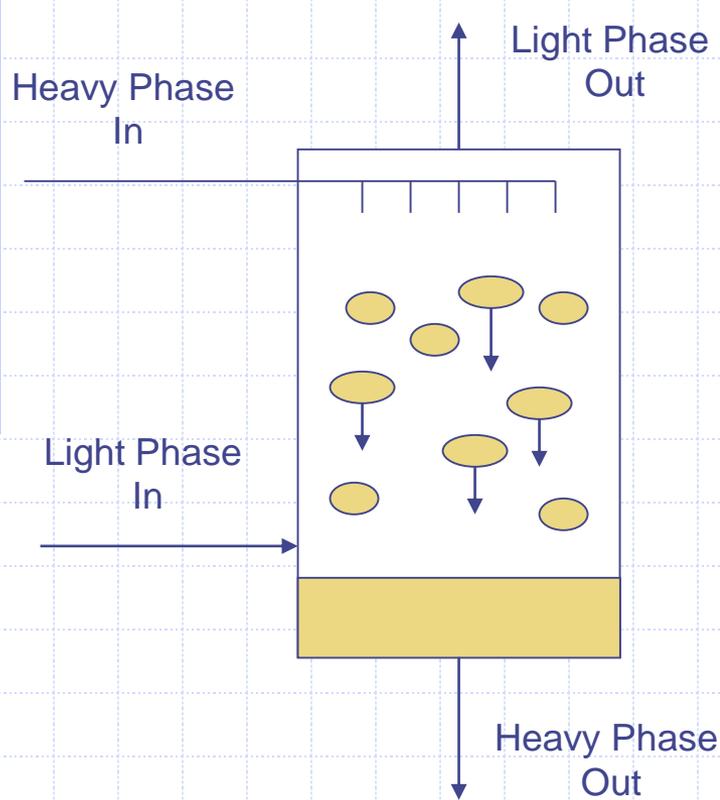
Solvent Extraction fundamentals

- ◆ One crucial choice for LL extraction is **solvent selection**.
- ◆ In general, the problem is the following:
 - a mixture is given (binary, for simplicity) containing a component that must be obtained with a certain degree of purity.
 - It is then attempted to transfer this component from the starting solution to a second solution (called the **extract**), which is obtained by adding a third component to the system: the solvent.
 - Alternately, it might be appropriate to extract the second component instead of the component of interest, which is then obtained as the residue of the extraction (called the **raffinate**).
- ◆ Similarly to absorption and stripping separation processes, the component of interest (after the extraction step) must be separated from the extract (or the raffinate) in a second process step, to achieve the desired degree of purity.
 - This second step, which can be a distillation or a precipitation (crystallization), is necessary to obtain the recovery and recycle of the solvent.

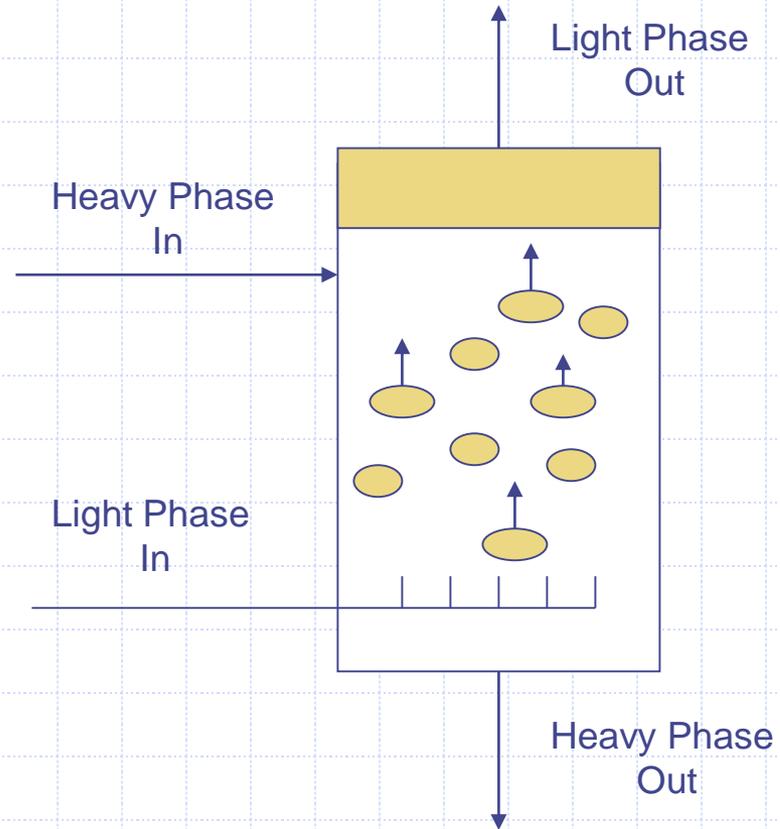
Desirable properties for the solvent selected for extraction

- ◆ **High solubility** towards the component to be extracted
 - to limit solvent consumption.
- ◆ **High selectivity** to extract substantially only one component from the starting solution.
- ◆ **Low solubility in the raffinate**, to limit solvent losses.
- ◆ **Good separability** of the extract
 - if distillation is used, it is desired to have a significant difference in boiling points and the absence of azeotropic conditions
- ◆ **Large difference in density** of the two liquid phases
 - to facilitate separation.
- ◆ Appropriate value of the **interfacial tension**:
 - a low value ensures small size of the drops, but facilitates the formation of emulsions;
 - a high value favors the coalescence, produces larger drops reducing the mass transfer.
- ◆ **Low viscosity**, as it favors mass transfer.
- ◆ **Low vapor pressure** at the extraction conditions,
 - to reduce evaporative losses.
- ◆ **Low cost and high availability.**
- ◆ **Chemical and thermal stability** and non-corrosive property.
- ◆ **No implications for safety and the environment.**

Typical Extractor



Heavy Phase Dispersed



Light Phase Dispersed



Binary liquid-liquid equilibrium

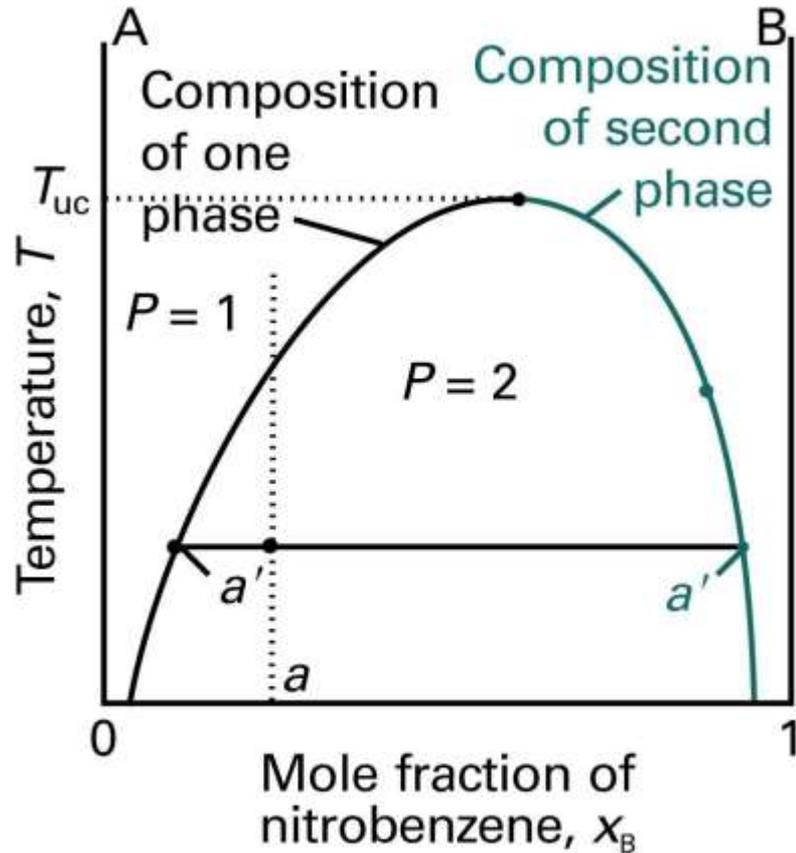


Figure 6-19
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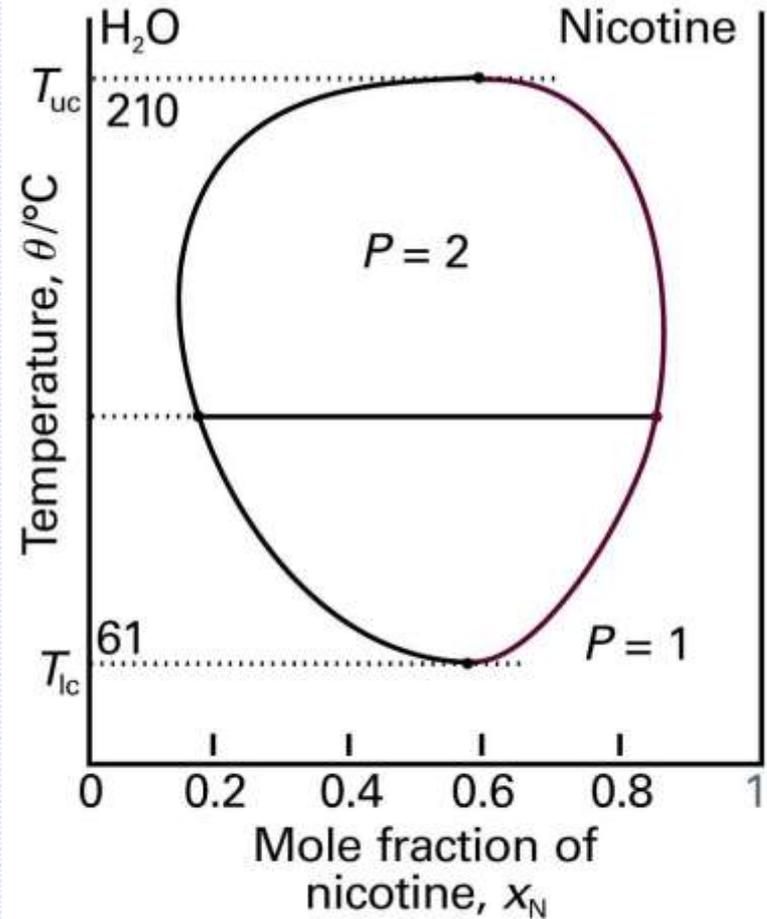


Figure 6-25
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Liquid-liquid equilibrium in presence of an azeotrope

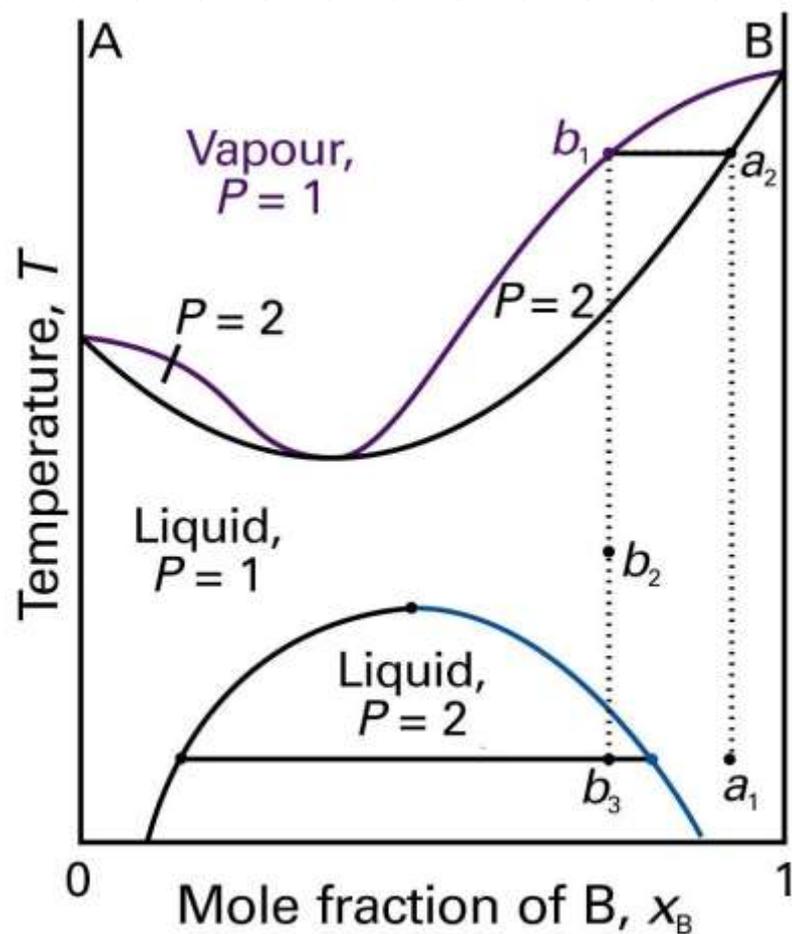


Figure 6-26
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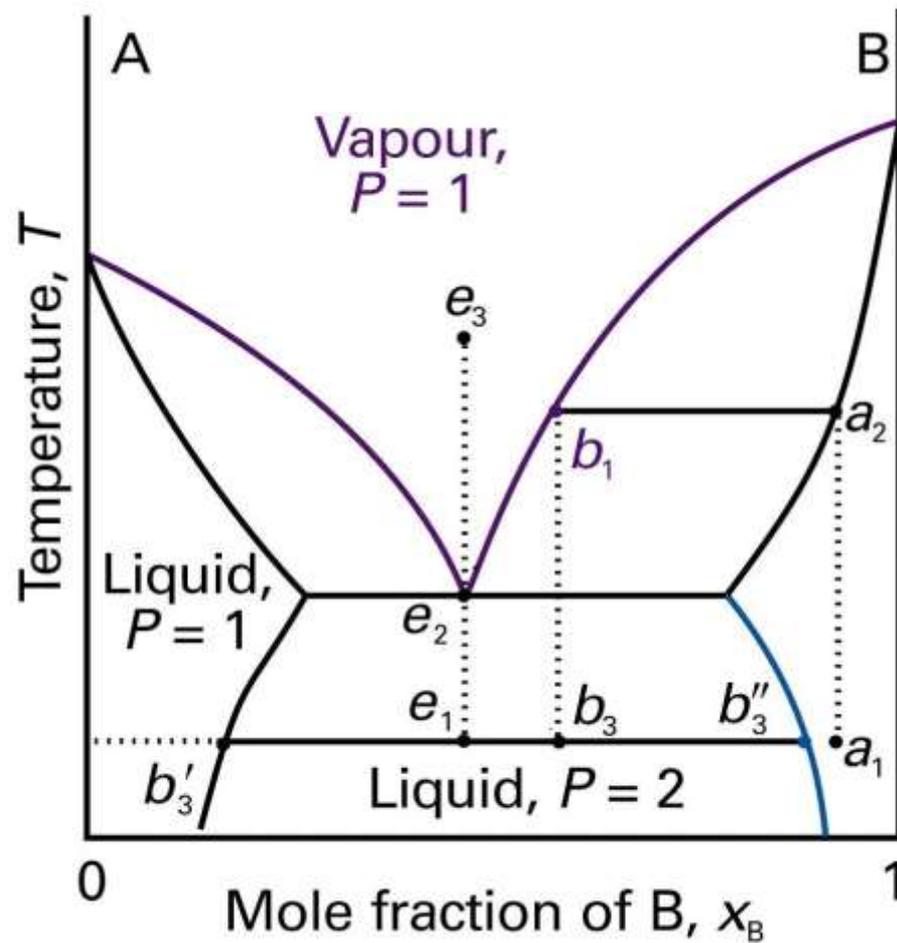
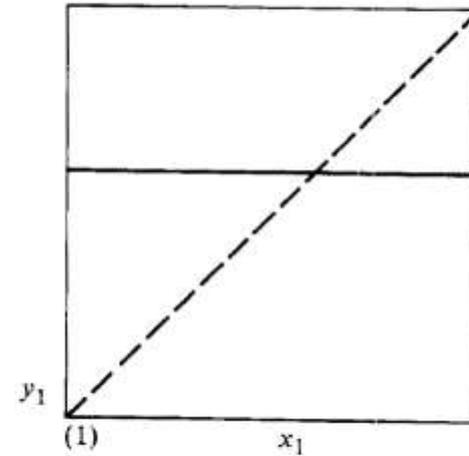
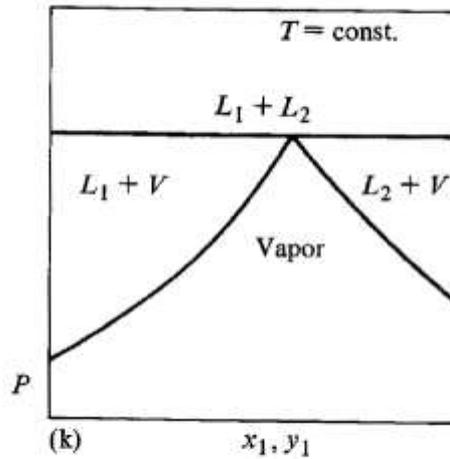
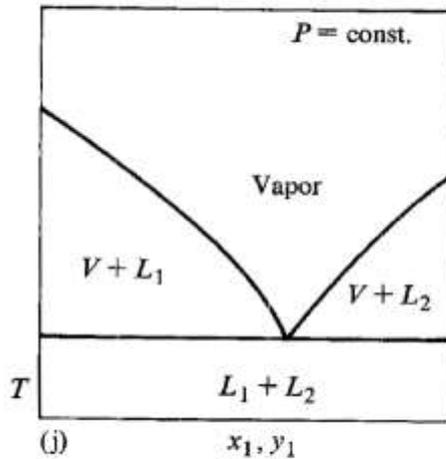


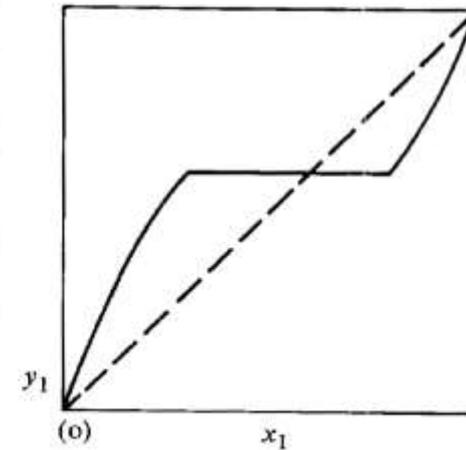
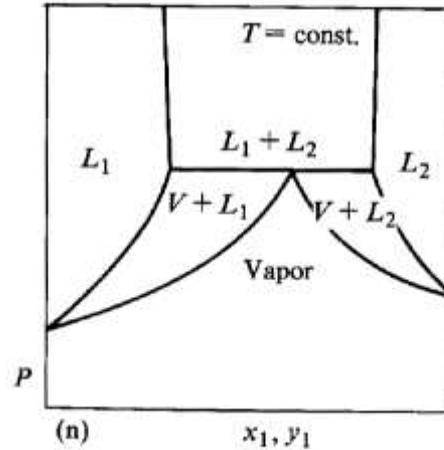
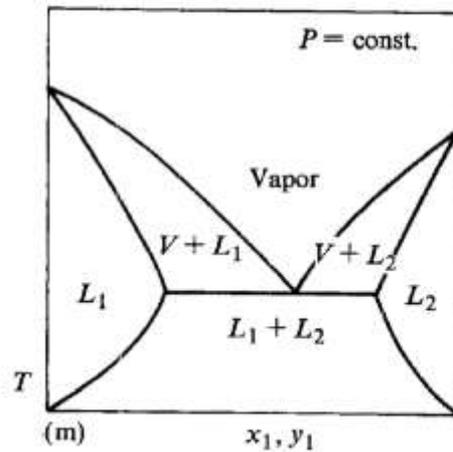
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T-x, p-x, and x-y diagrams of various types

IV. Systems having immiscible liquid phases



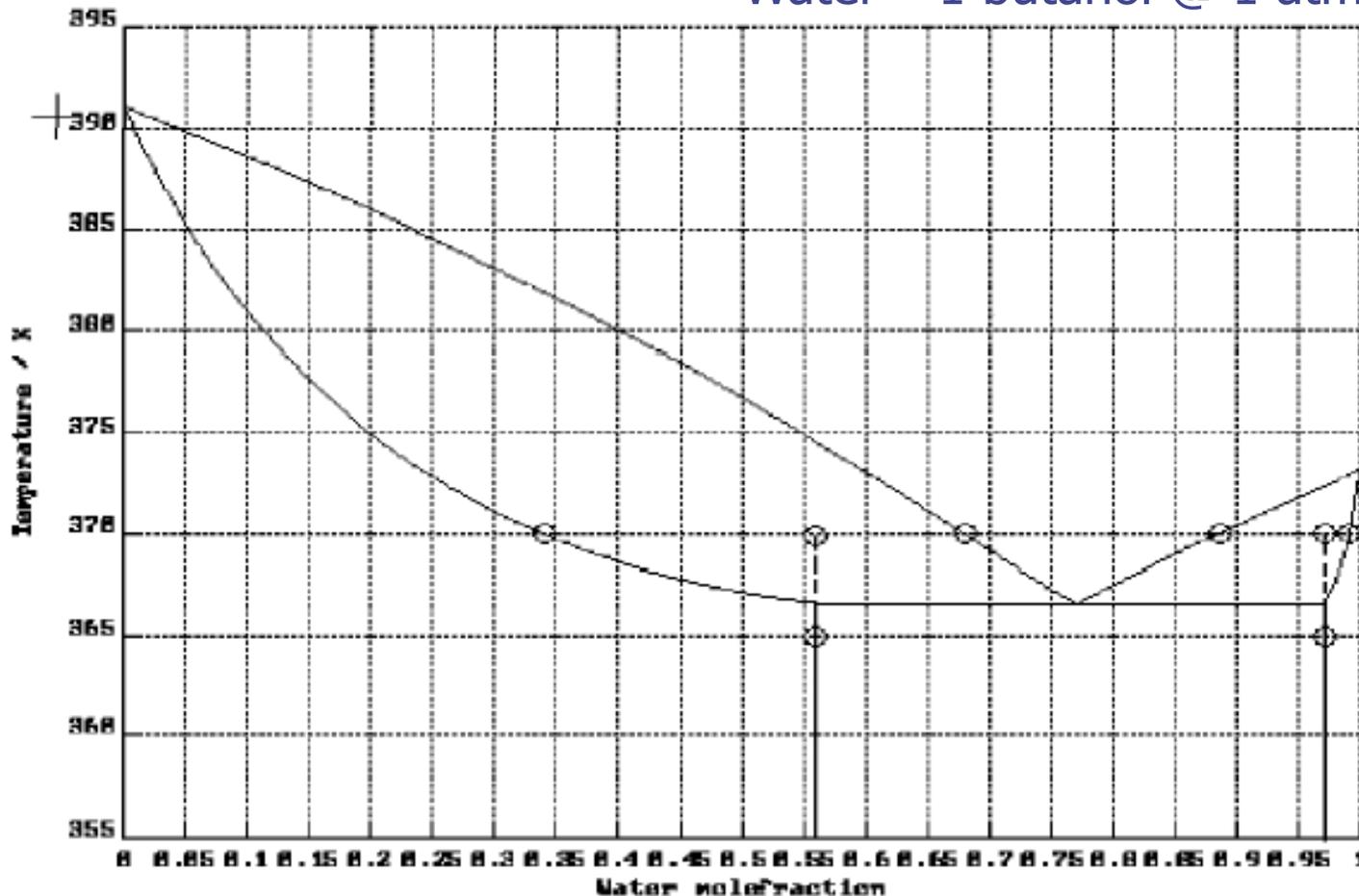
V. Systems having partially miscible liquid phases



Liquid Liquid and VLL equilibrium

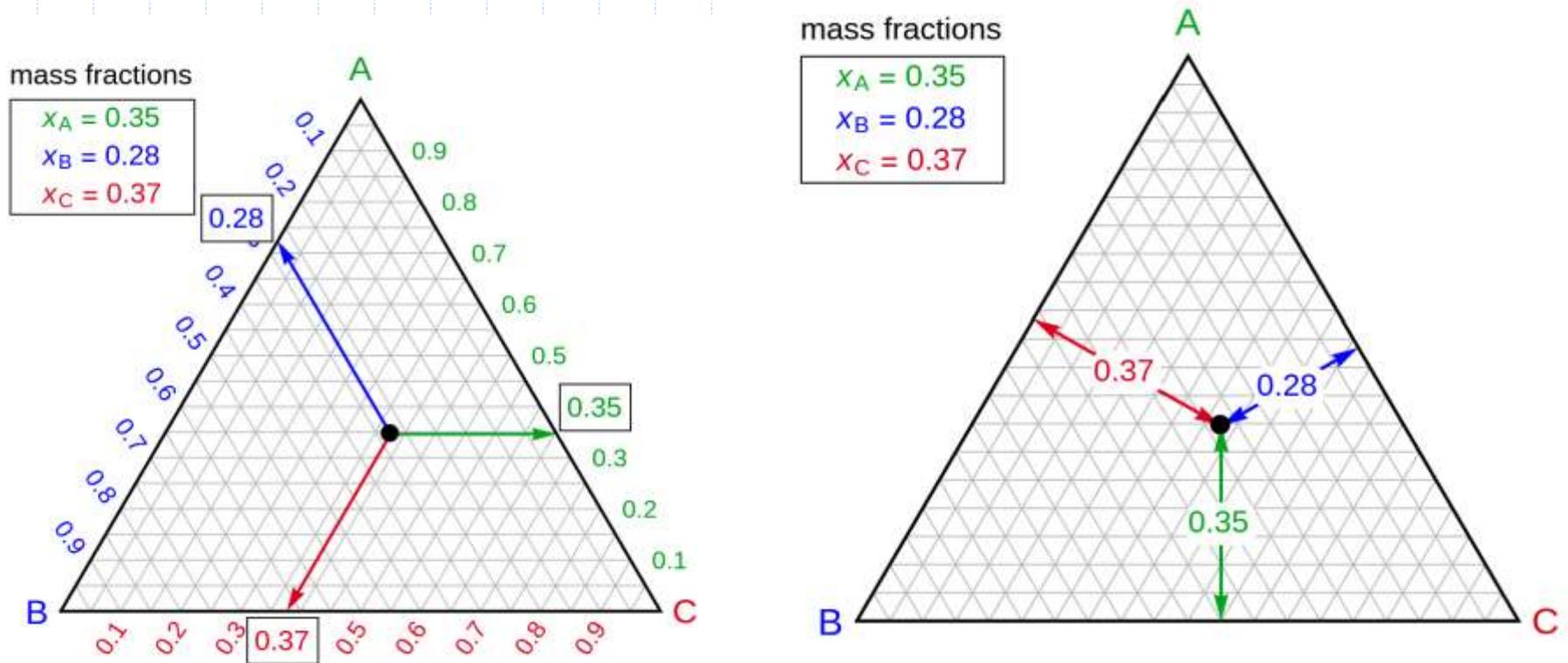
◆ The basic VLLE equation is $P y_i \hat{\phi}_i^V = f_i^{o1} x_i^1 \gamma_i^1 = f_i^{o2} x_i^2 \gamma_i^2$

Water – 1 butanol @ 1 atm



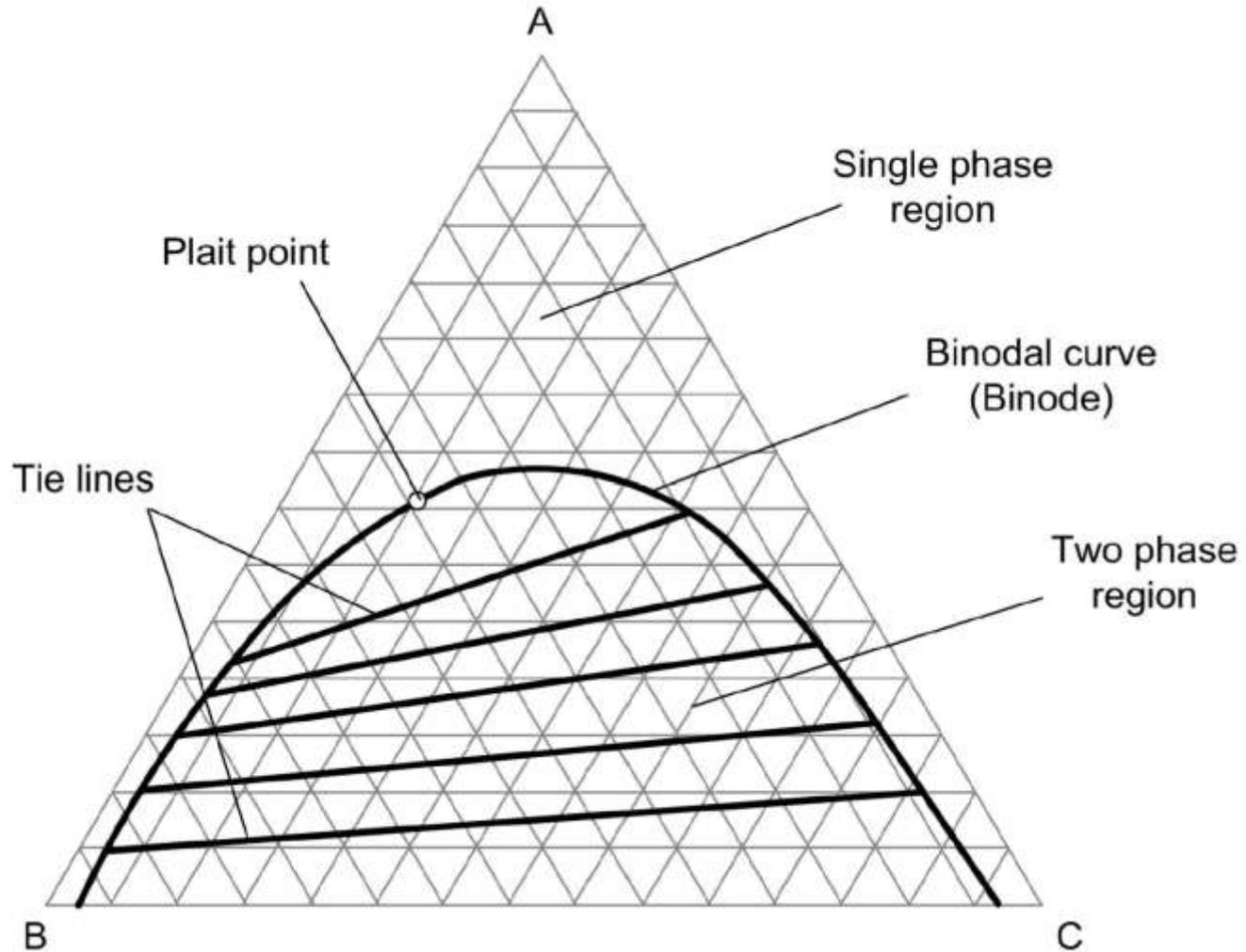
Ternary LLE phase diagrams

- ◆ Two alternative ways of reading compositions (mole or mass) in triangular diagrams



Ternary LLE phase diagrams

- ◆ A typical LLE ternary phase diagram (type I)

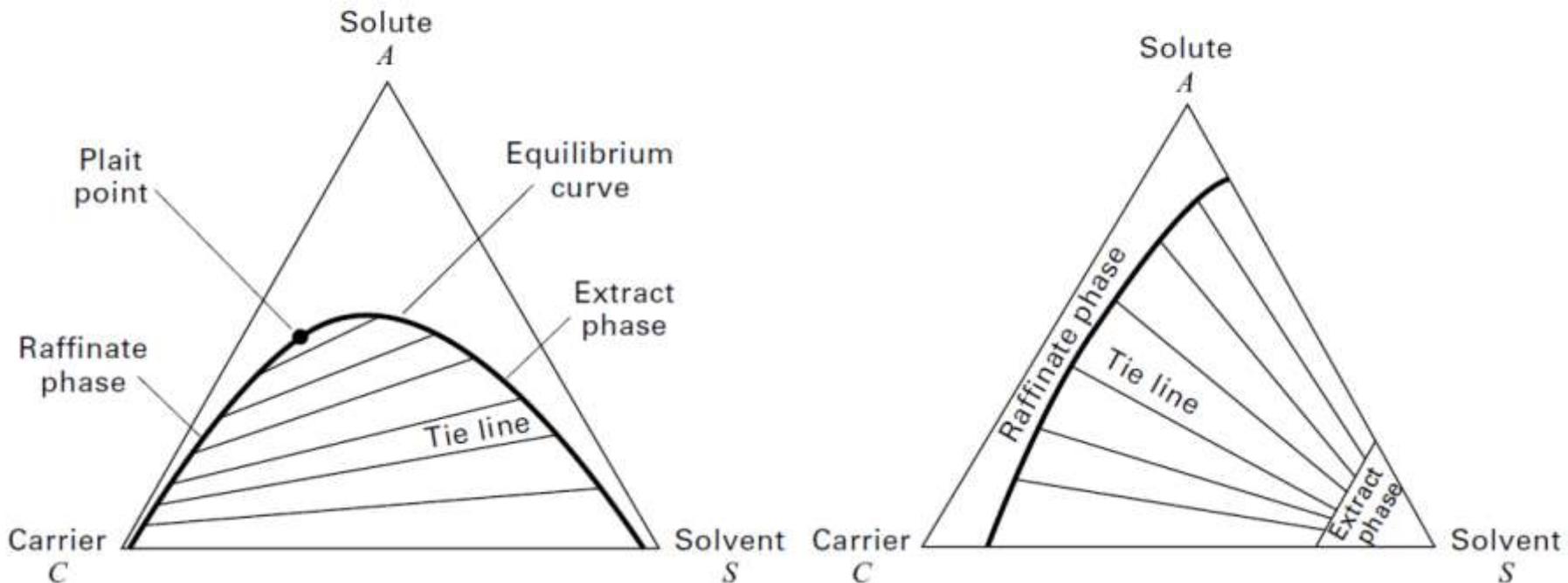


Ternary LLE phase diagrams

- ◆ At constant T and P one or two binary systems may show a miscibility gap: they are referred to as "Type I" and "Type II" systems.
- ◆ The two branches of the solubility curves refer to phase α (solutions with low S content) and to phase β (solutions with high S content).

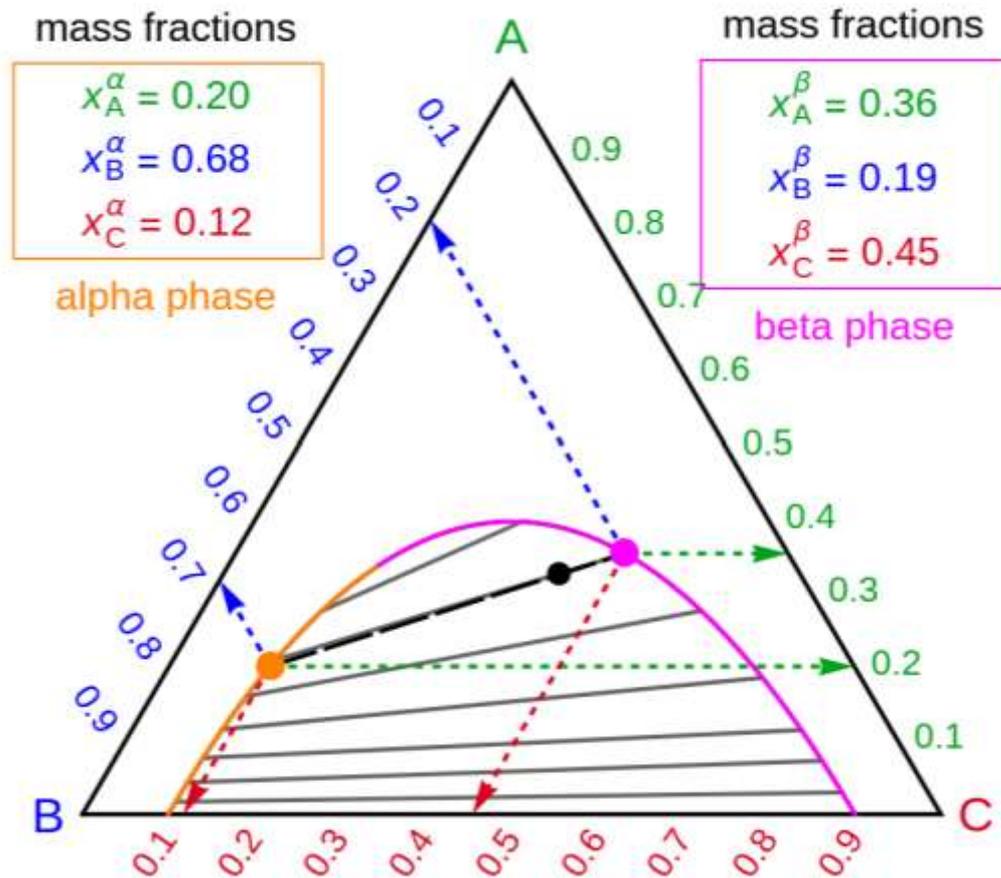
Type I: One immiscible pair

Type II: Two immiscible pairs



Triangular LLE phase diagrams

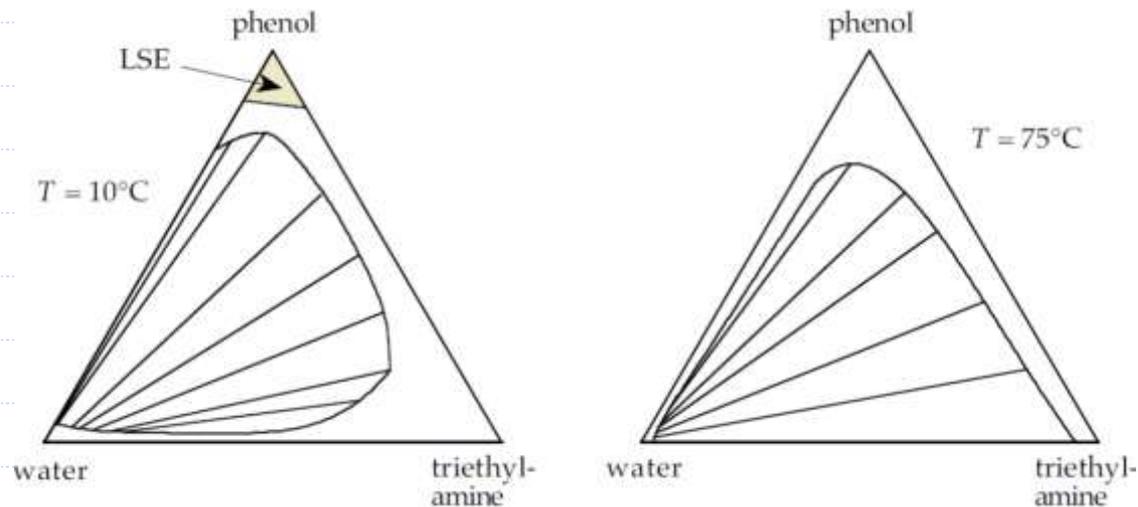
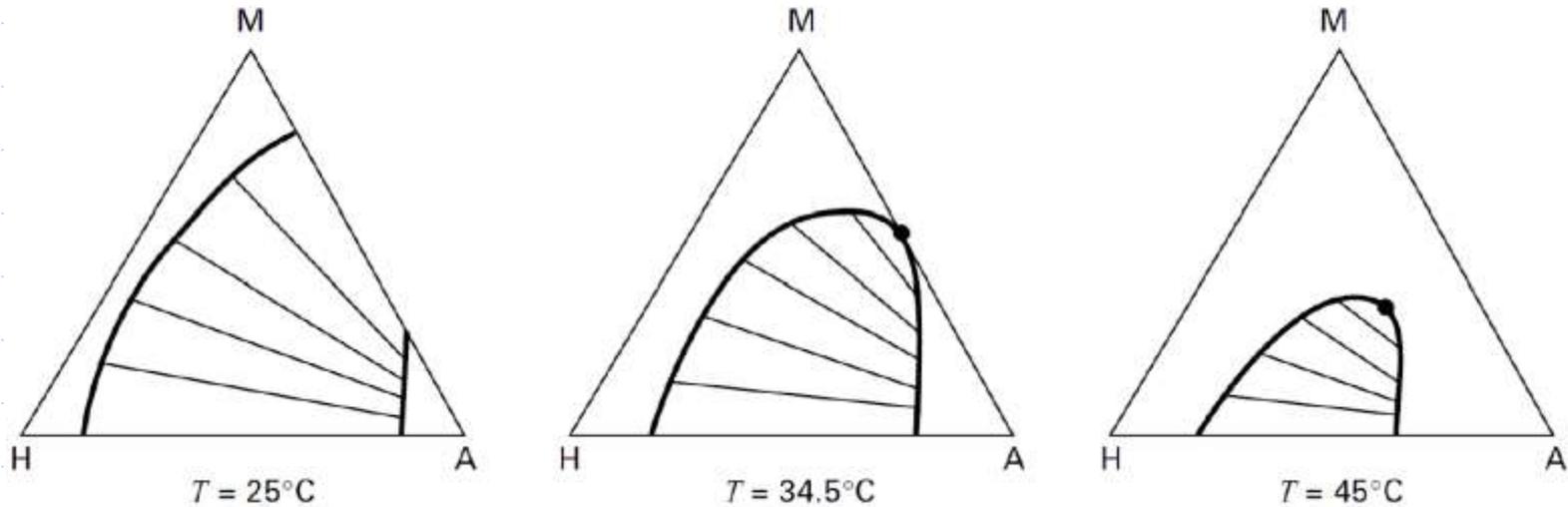
- ◆ How to read compositions inside the miscibility gap



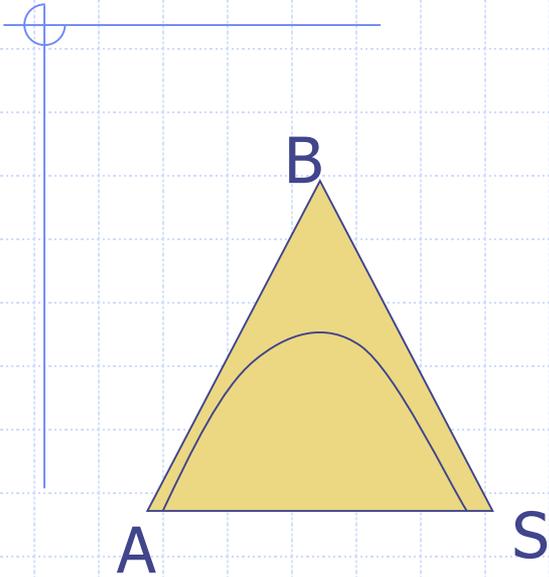
Run Demo

Effect of temperature on miscibility for ternary mixtures

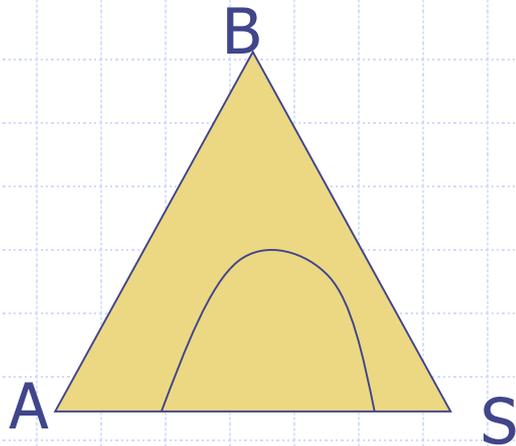
n-hexane (H)/methylcyclopentane (M)/aniline (A)



Insolubility of solvent



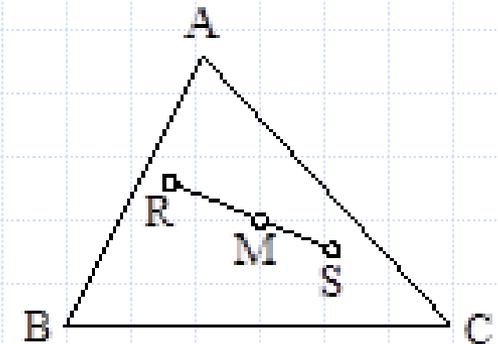
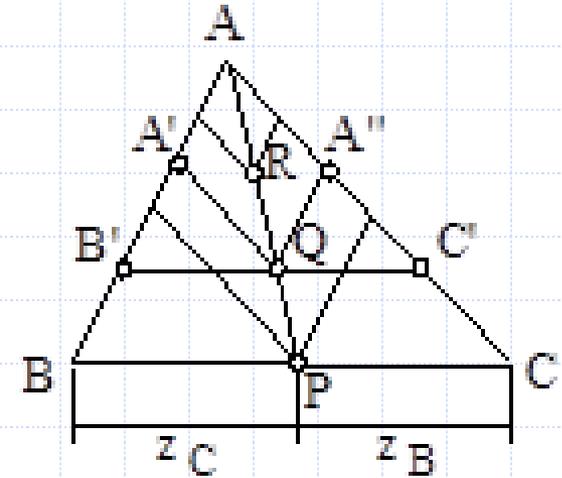
Preferred solvent – A and S have limited solubility



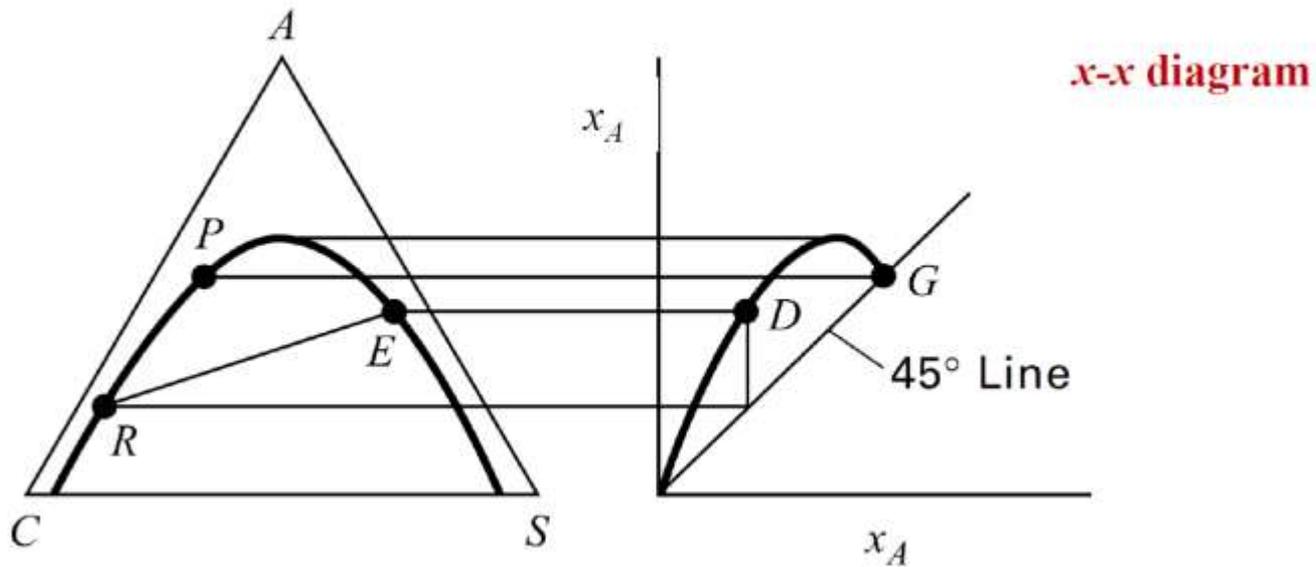
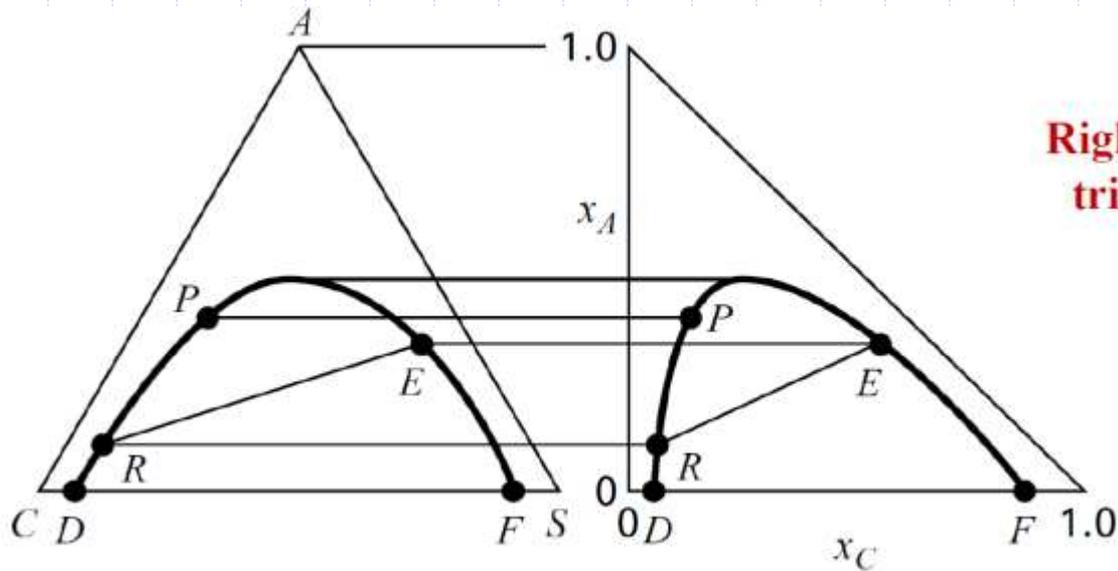
S very soluble in A and A very soluble in S

Representing a ternary system: ternary diagrams

- ◆ Points P, Q and R, belonging to the segment AP, coming out from vertex A, are characterized by the constant value of the z_B/z_C ratio
 - This is immediately shown by the similarity of the triangles which identify the fraction of these components on the sides AB and AC.
 - Also the segments QC' and QB' , on the parallel to BC passing through Q, are in the same ratio.
- ◆ Mixing of mixtures R and S to obtain mixture M is shown in figure.
 - Point M on the segment RS divides it into parts proportional to the respective quantities according to the lever rule.



Alternative ternary LLE diagrams



Using a pseudo-binary representation of LLE

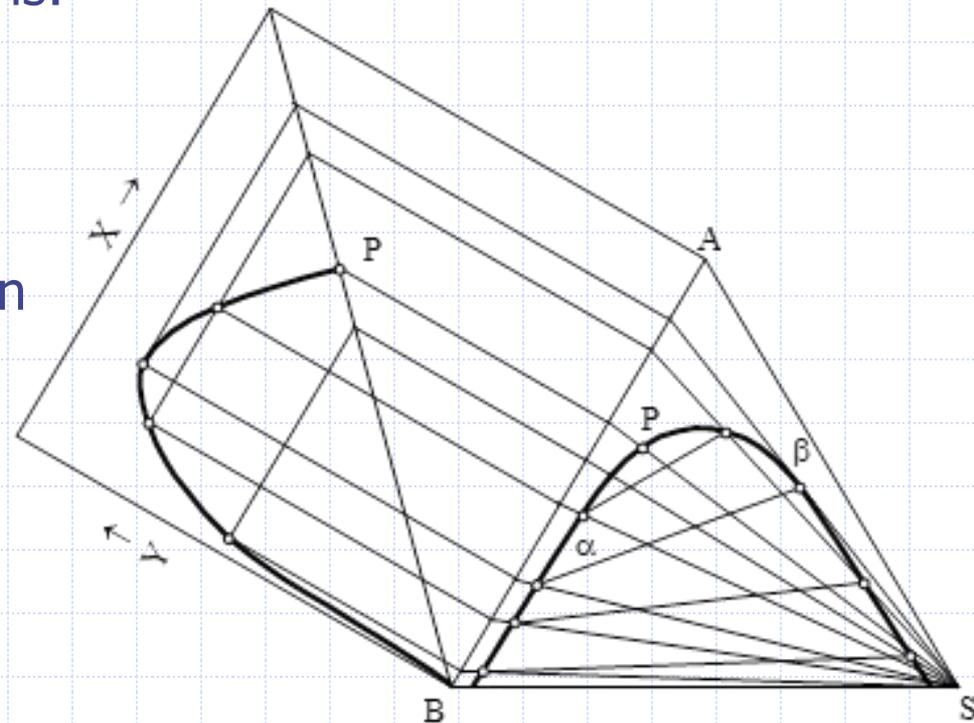
- ◆ In the pseudo-binary representation the solvent is not accounted for (solvent free representation). The pseudo-binary fractions are defined by:

$$X_A = \frac{x_A^\alpha}{x_A^\alpha + x_B^\alpha}; \quad X_B = 1 - X_A \quad Y_A = \frac{x_A^\beta}{x_A^\beta + x_B^\beta}; \quad Y_B = 1 - Y_A$$

- ◆ Selectivity of A with respect to B is:

$$S_{AB} = \frac{Y_A/Y_B}{X_A/X_B} = \frac{x_A^\beta/x_B^\beta}{x_A^\alpha/x_B^\alpha}$$

- ◆ The pseudo-binary representation does not completely define equilibrium. In order to draw the equilibrium curve, two more pseudo-binary diagrams are required.



Using Janecke representation of LLE

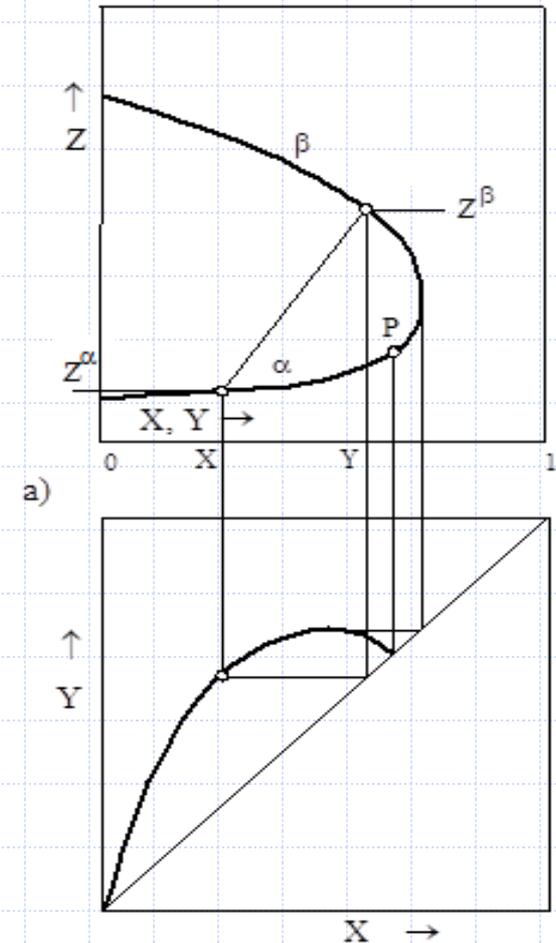
- ◆ The abscissa reports the pseudo-binary compositions of the phases in equilibrium.

$$X_A = \frac{x_A^\alpha}{x_A^\alpha + x_B^\alpha}; \quad X_B = 1 - X_A$$

$$Y_A = \frac{x_A^\beta}{x_A^\beta + x_B^\beta}; \quad Y_B = 1 - Y_A$$

- ◆ The ordinate reports the ratios between the amount of solvent S and that of the binary system AB in the phase considered:

$$Z = \frac{x_S}{x_A + x_B}$$



Evaluating LLE in ternary system

- ◆ In a three-component system with two co-existing liquid phases three iso-activity conditions can be written to calculate the thermodynamic equilibrium:

$$f_1^\alpha = f_1^\beta$$

$$f_2^\alpha = f_2^\beta$$

$$f_3^\alpha = f_3^\beta$$



$$(x_i P_i^0 \gamma_i)^\alpha = (x_i P_i^0 \gamma_i)^\beta$$

$$(x_i \gamma_i)^\alpha = (x_i \gamma_i)^\beta$$

Phase I

Phase II

- ◆ NRTL and UNIQUAC can be used for activity coefficients.
- ◆ Distribution coefficients $K = y/x$ are defined

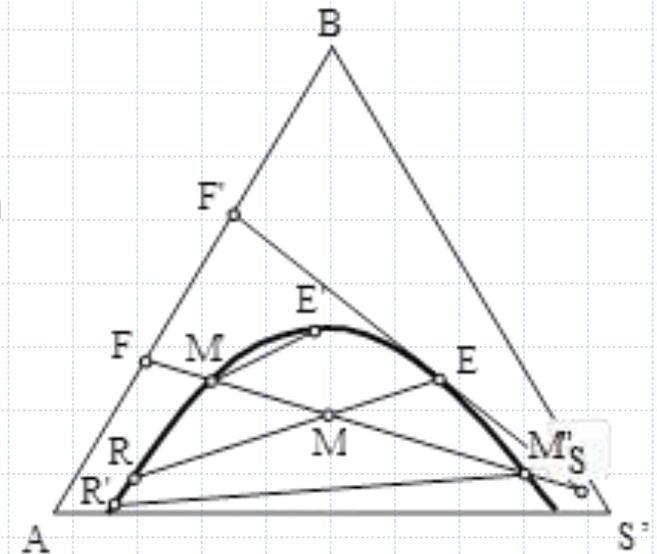
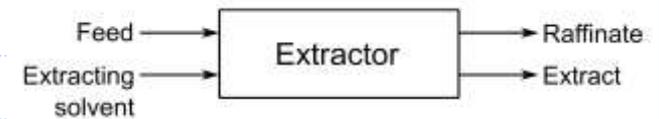
Single stage operation: the mixer-settler process

◆ In a ternary diagram, knowing the ratio F/S , point M is determined on the FS segment

- dividing into parts proportional to F and S (lever rule).
- Point M represents the total outlet stream.
- Points R and E are on the tie line passing through M , and it results $R/E = ME/RM$.
- M' and M'' are the maximum and minimum values of the F/S ratio that allow the separation of the A and S mixture into two phases

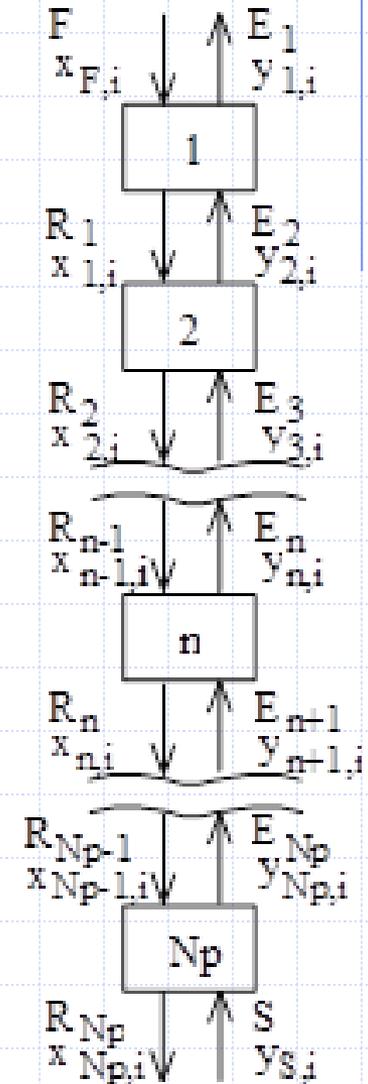
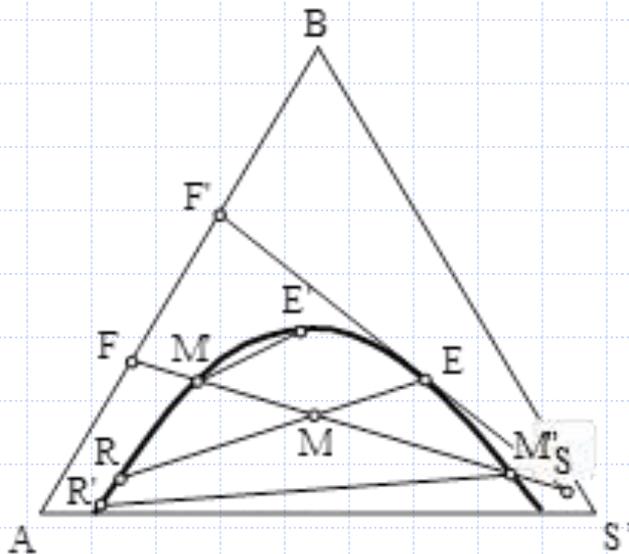
◆ NOTE:

- another complication of solvent extraction is the need to separate an emulsion of two liquid phases after extraction has been carried out.
- This is usually achieved by **gravity settling**. In a mixer-settler system it is assumed that that the two outlet streams are in thermodynamic equilibrium with each other.



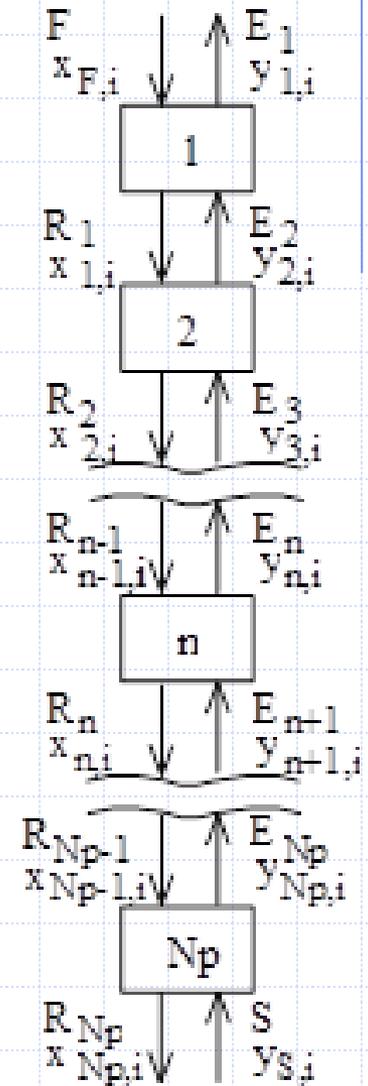
Multi-stage countercurrent operation: mixer-settler in series

- ◆ A mixer-settler system has insufficient performances.
 - Limit values for the extract (phase E' , in equilibrium with M') and for the raffinate (phase R' , in equilibrium with M'') are evidenced.
 - Also the compositions of E and R are limited by thermodynamics.
- ◆ A number of mixer-settler in series, connected countercurrently,
 - is a possible way to overcome this problem.



Multi-stage countercurrent operation: degrees of freedom

- ◆ Another limitation of a mixer-settler system is that it has only one degree of freedom.
 - Using a number of mixer-settler in series, connected countercurrently, leads to a system which is similar to absorption and stripping multistage units.
- ◆ Accordingly, a multiple mixer-settler system has two degrees of freedom (**design**) and one degree of freedom (**rating**).
 - A design specification on the extract (or on the raffinate) is selected as one of them.
 - The second one is usually the inlet solvent flow rate.
- ◆ As a **non-thermal separation process**, Solvent Extraction has no energy duties, and is performed at ambient temperature and pressure.



Multi-stage countercurrent operation: material balances

- ◆ Overall material balances:

$$F + S = M = E_1 + R_{Np}$$

$$F x_{F,i} + S y_{S,i} = M x_{M,i} = E_1 y_{1,i} + R_{Np} x_{Np,i}$$

- ◆ Section of stages above stage n :

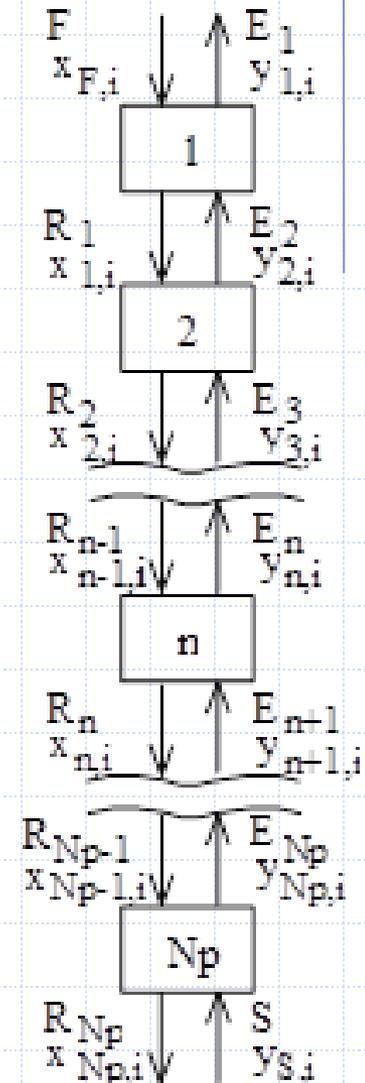
$$R_{n-1} + S = E_n + R_{Np}$$

$$R_{n-1} x_{n-1,i} + S y_{S,i} = E_n y_{n,i} + R_{Np} x_{Np,i}$$

- ◆ These balance equations can be rewritten in the form:

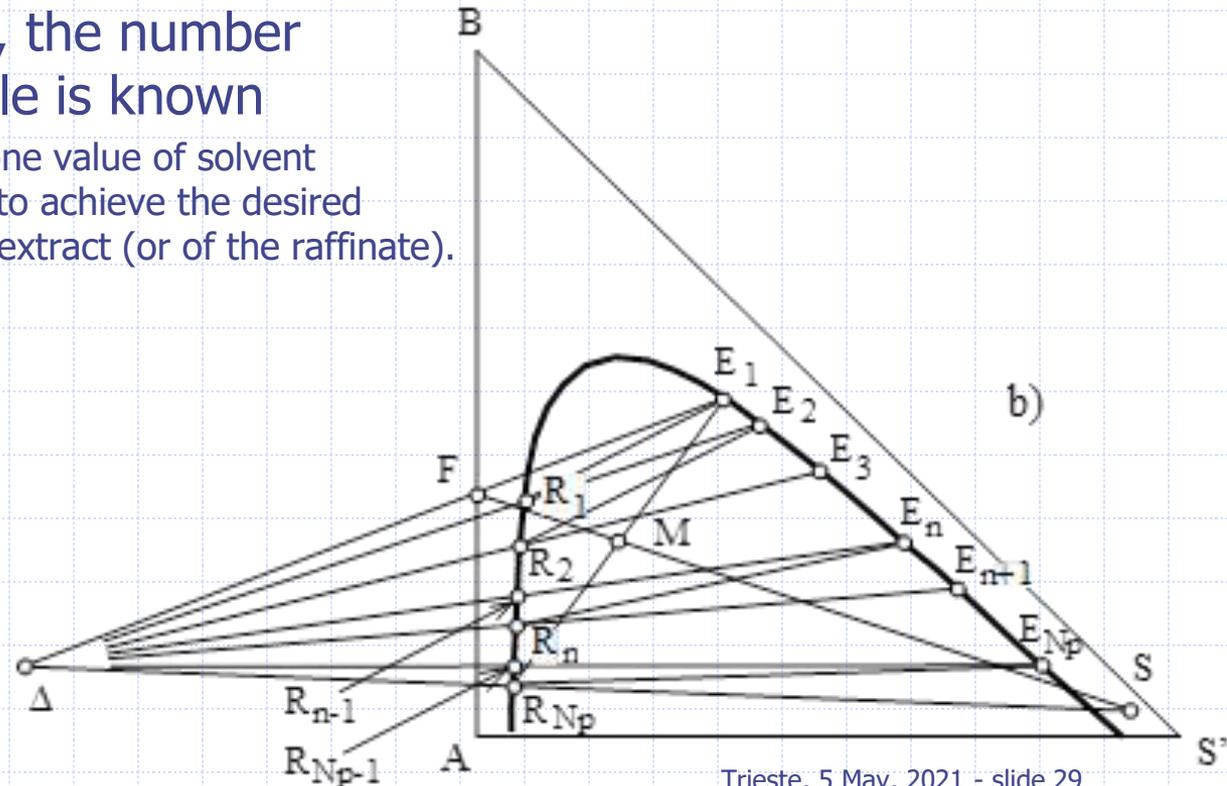
$$R_{Np} - S = F - E_1 = R_{n-1} - E_n = \Delta$$

- and they define point Δ , which is aligned with points R_{Np} and S , as well as with points F and E_1 ,
 - indicating that all the balance operating lines go through pole Δ .
- ◆ The construction of the number of ideal stages required for separation is immediate, and the number of stages required corresponds to the tie lines drawn.



Multi-stage countercurrent operation: number of stages

- ◆ The construction of the number of stages is represented in the figure.
- ◆ In a **design** calculations, flow rates F and S , and feed and solvent composition are known.
 - The composition of the extract, or that of the raffinate, is fixed as a design specification.
 - The number of ideal stages required for separation is calculated from E_1 , and using equilibrium or balance equations, alternately.
- ◆ In **rating** calculations, the number of ideal stages available is known
 - so that there will be only one value of solvent flow rate S which ensures to achieve the desired output composition of the extract (or of the raffinate).



Counter-current graphical solution: 2 units

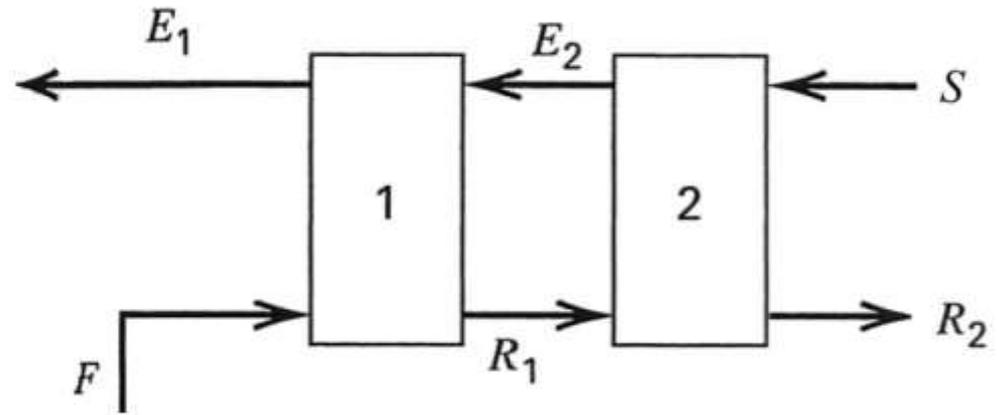
$$F + E_2 = E_1 + R_1$$
$$E_2 + R_2 = S + R_1$$

Rearrange:

$$F - E_1 = R_1 - E_2$$

$$R_1 - E_2 = R_2 - S$$

$$(F - E_1) = (R_1 - E_2) = (R_2 - S) = \mathbf{P}$$



Note:

each difference is equal to P

Rearranging again:

$$F = E_1 + P$$

$$R_1 = E_2 + P$$

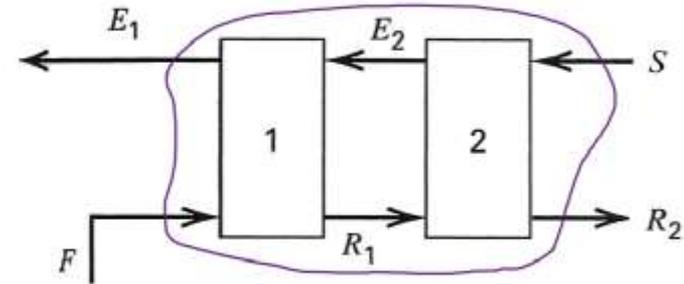
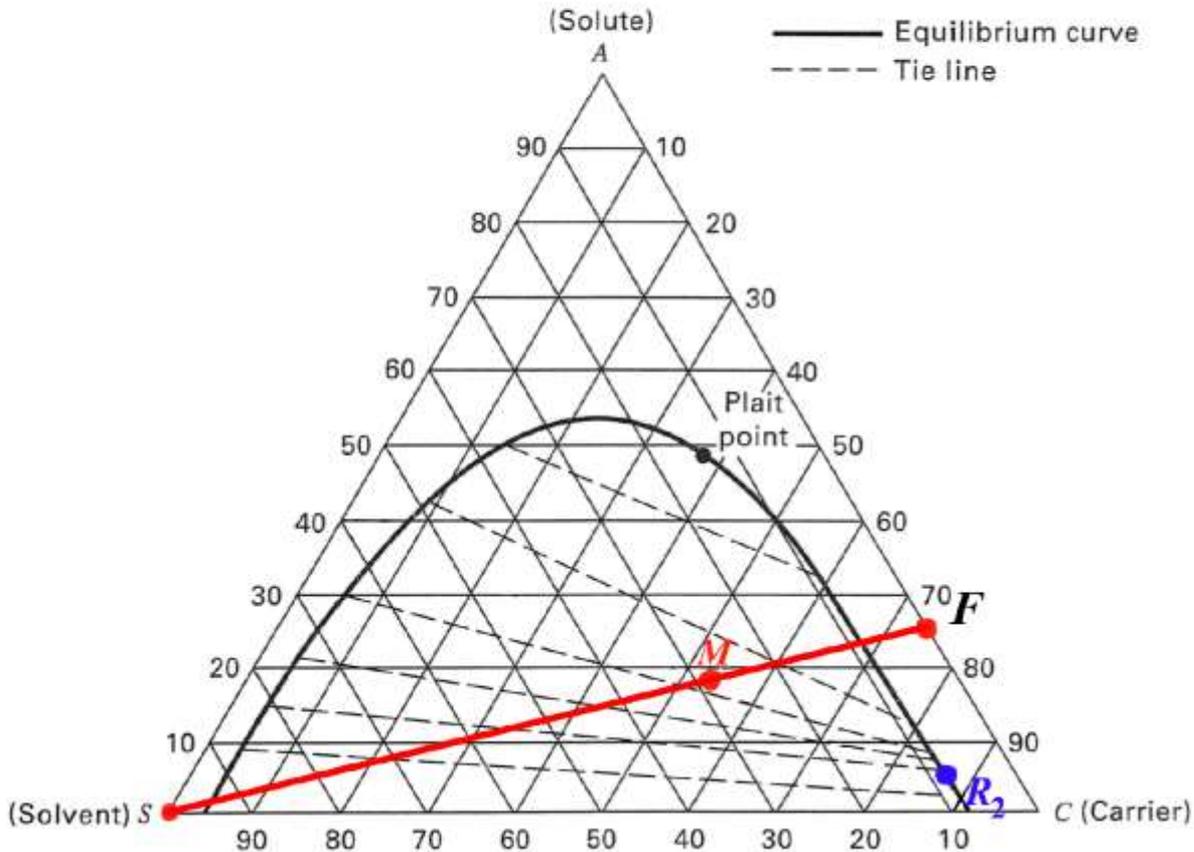
$$R_2 = S + P$$

Interpretation:

P is a fictitious operating point on the ternary diagram (from lever rule)

- F is on the line that connects E_1 and P
- R_1 is on the line that connects E_2 and P
- R_2 is on the line that connects S and P

Counter-current graphical solution: 2 units

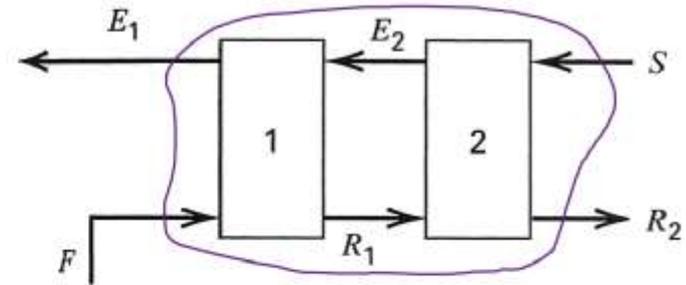
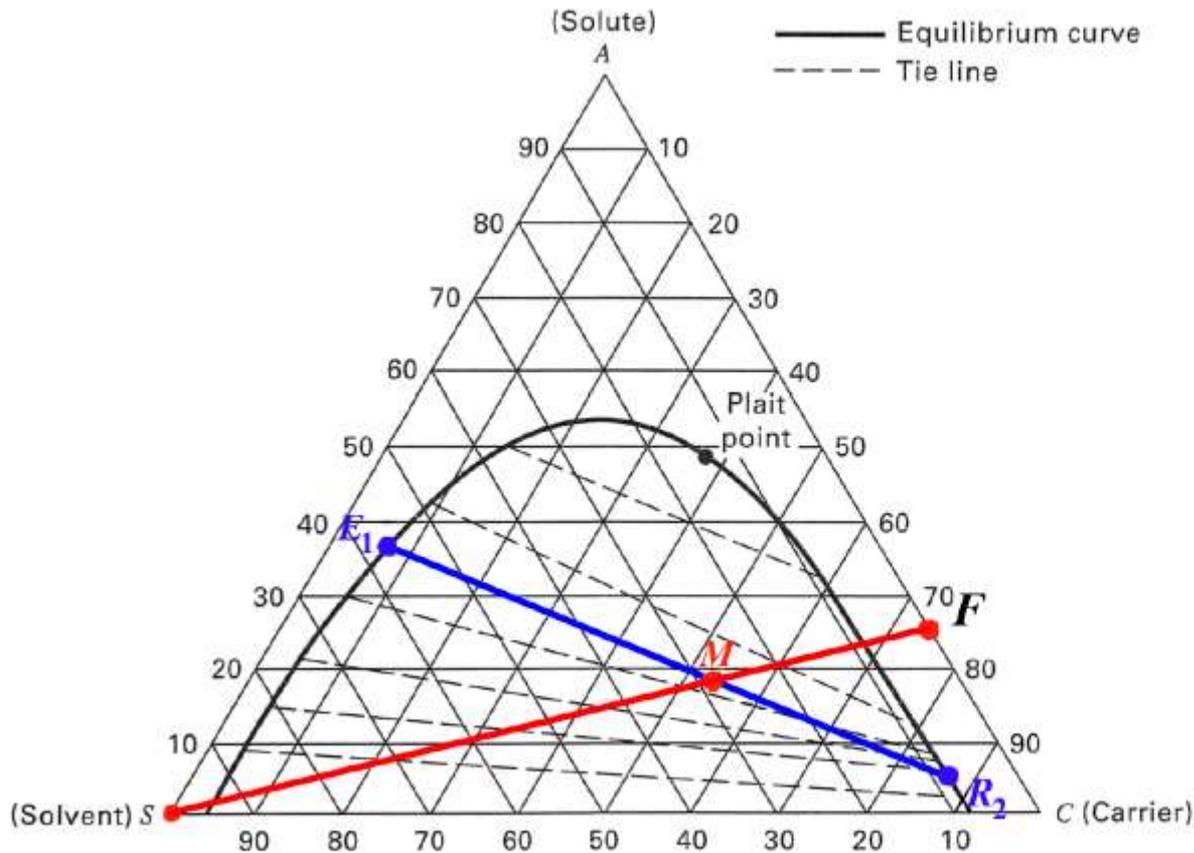


Feed	Solvent
$F = 250 \text{ kg}$	$S = 100 \text{ kg}$
$x_{F,A} = 0.24$	$x_{S,A} = 0.0$
$x_{F,C} = 0.76$	$x_{S,C} = 0.0$
$x_{F,S} = 0.00$	$x_{S,S} = 1.0$

Overall balance gives:

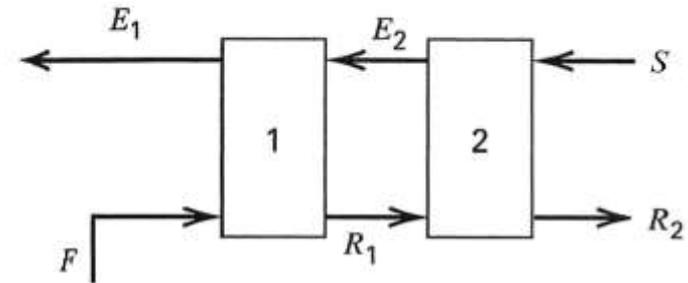
$$M = S + F = E_1 + R_2$$

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 .

Counter-current graphical solution: 2 units



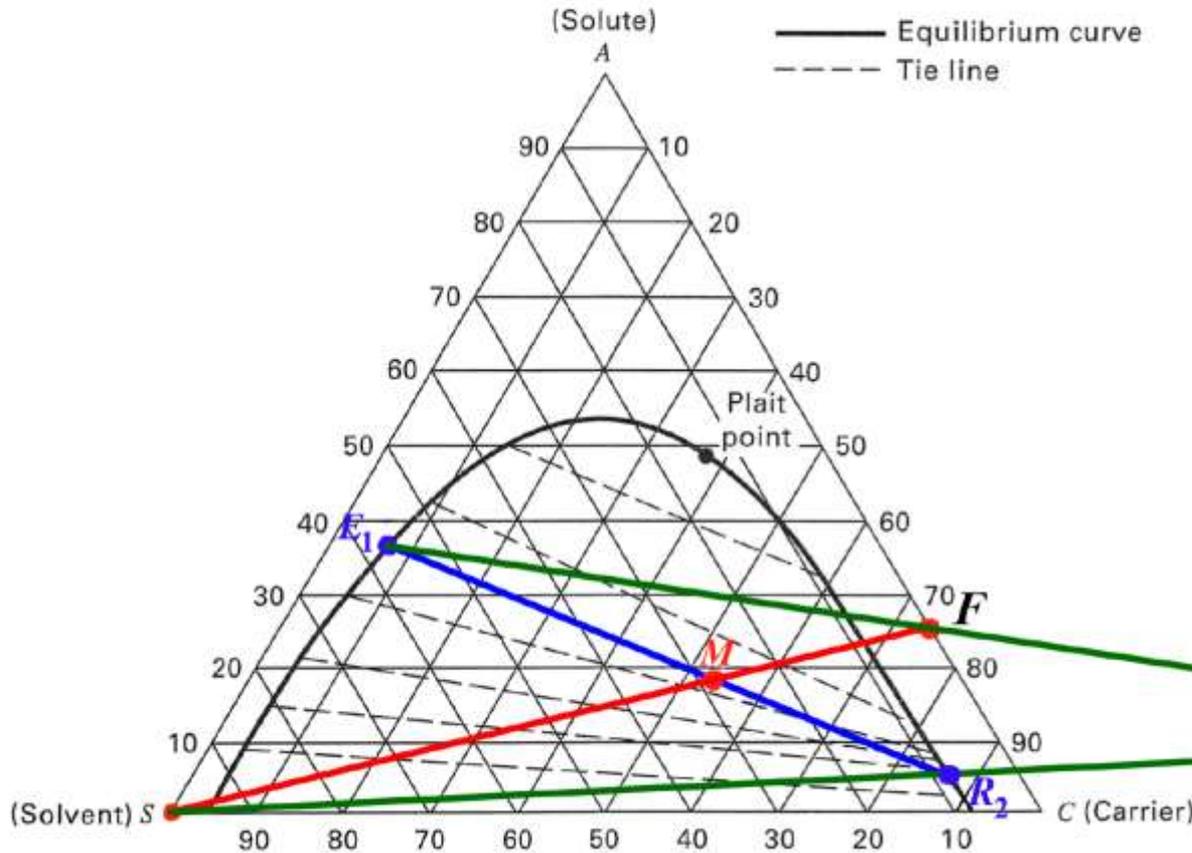
Recall:

$$F = E_1 + P$$

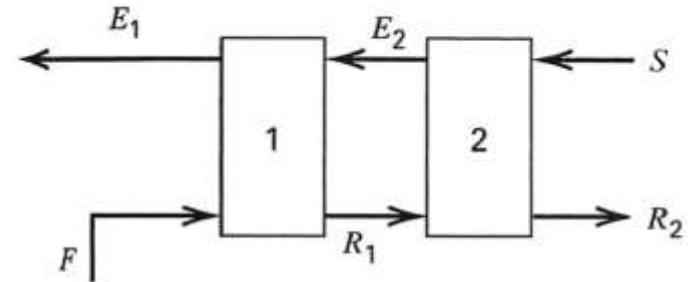
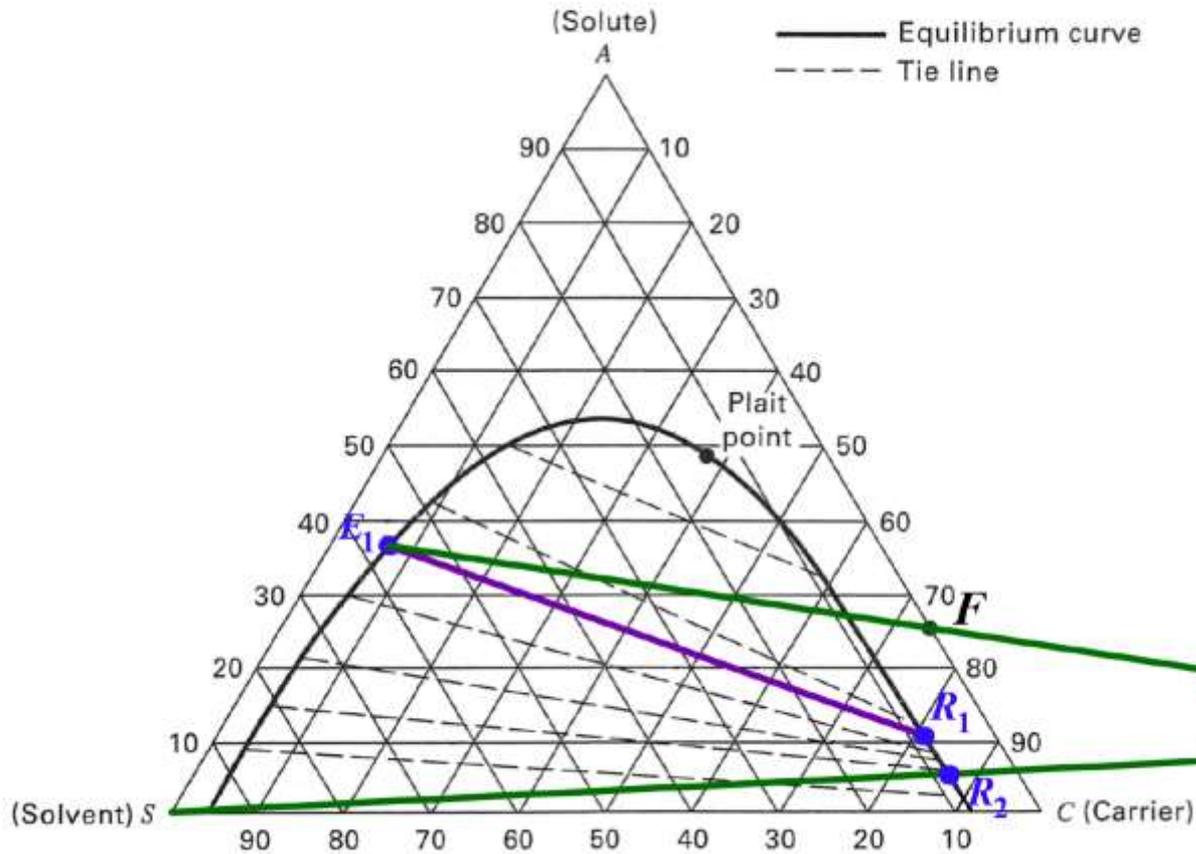
F is on the line that connects *E*₁ and *P*

$$R_2 = S + P$$

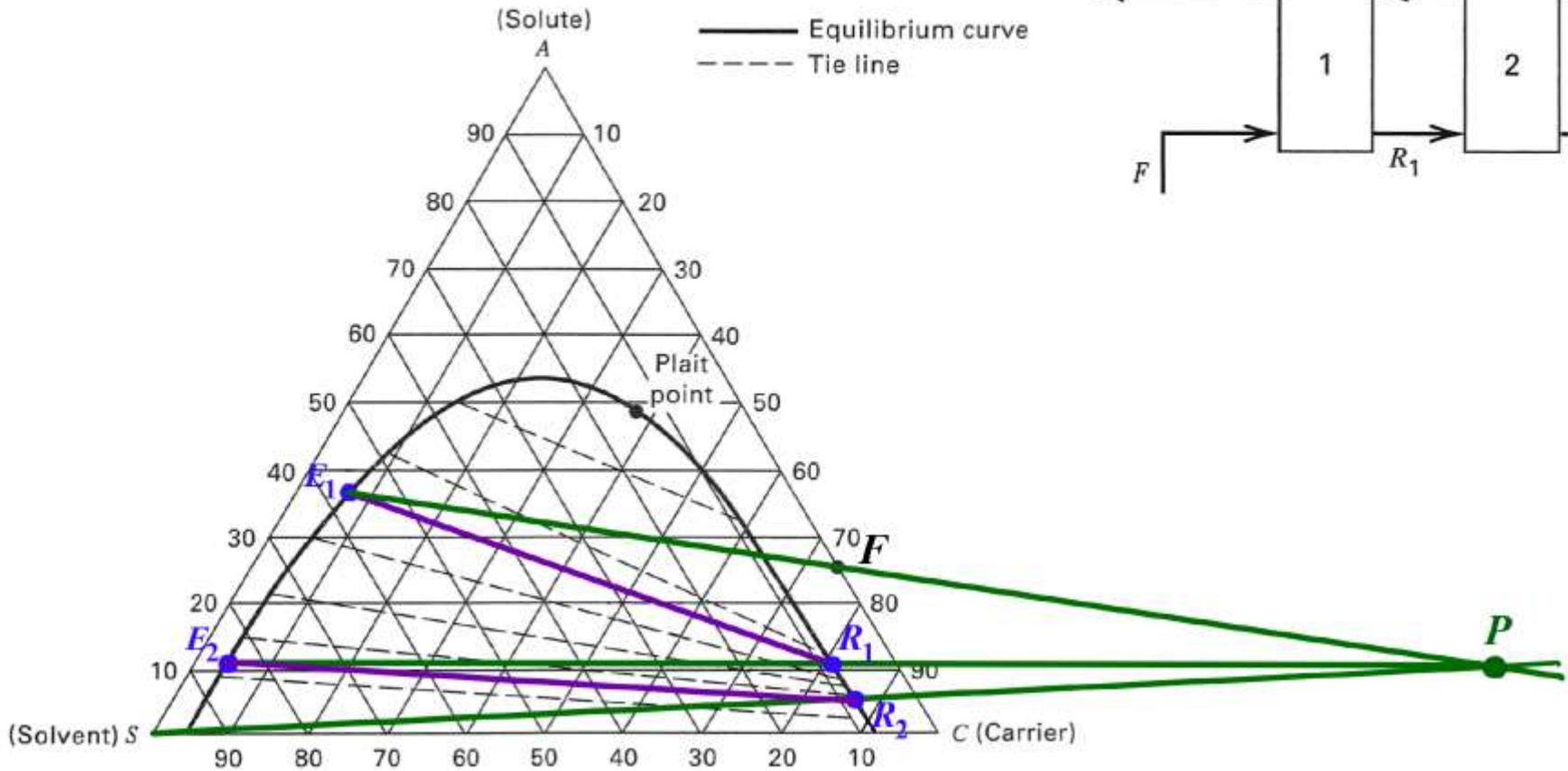
*R*₂ is on the line that connects *S* and *P*



Counter-current graphical solution: 2 units



Counter-current graphical solution: 2 units



In general....

$$F + E_2 = E_1 + R_1$$

$$E_2 + R_2 = E_3 + R_1$$

$$E_n + R_n = E_{n+1} + R_{n-1}$$

Rearrange:

$$F - E_1 = R_1 - E_2$$

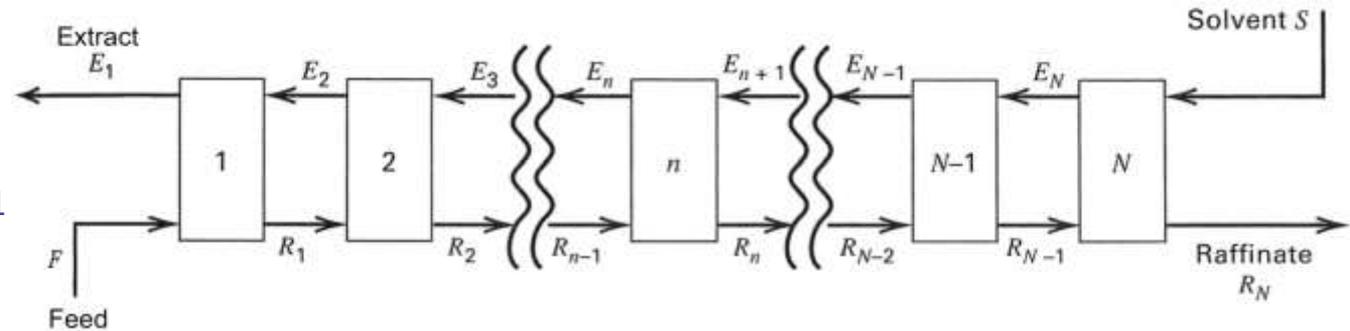
$$R_1 - E_2 = R_2 - E_3$$

$$R_{n-1} - E_n = R_n - E_{n+1}$$

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

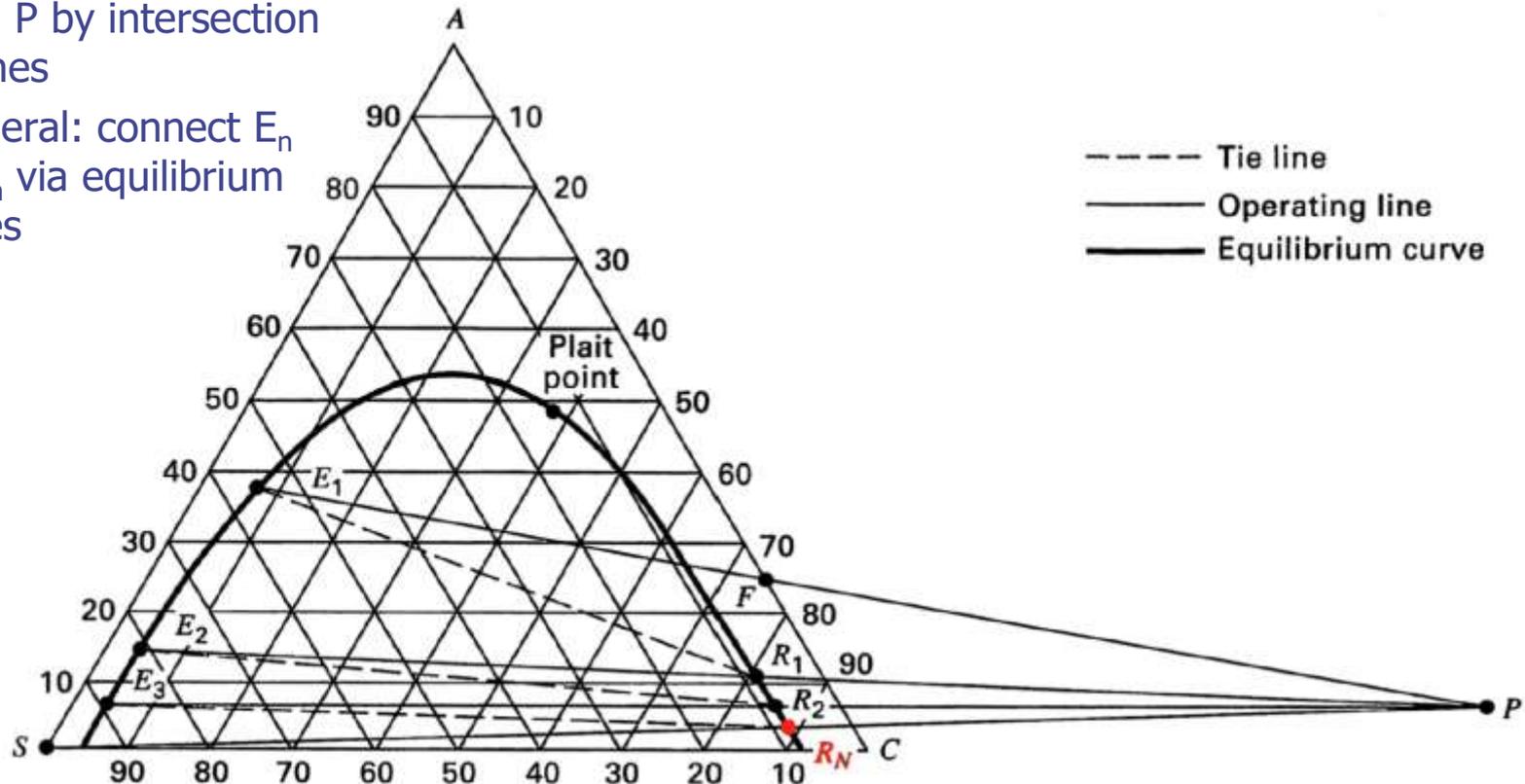
Notes:

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]



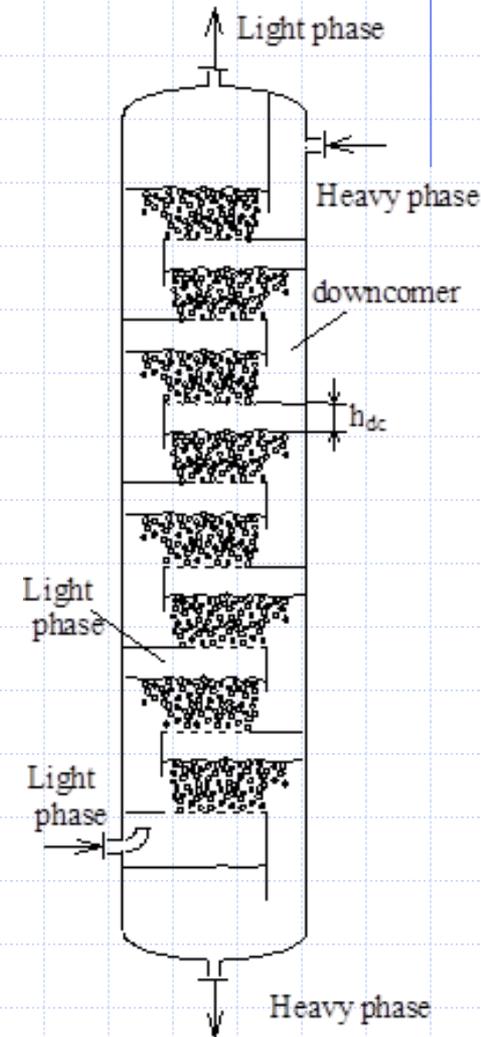
Counter current graphical solution: procedure

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



Multi-stage mixer-settler in a solvent extraction column

- ◆ A multi-stage mixer-settler system can be realized in a countercurrent column,
 - which can be a tray (sieve trays), as well as a packed column
- ◆ The solvent is fed to the bottom (if it has smaller density than the mixture to extract) or to the top (if its density is larger than the one of the mixture).
 - In this respect, solvent extraction can be assimilated to an absorption process (first case), or to a stripping process (second case).
- ◆ However, owing to the poorer mass transfer properties in liquid-liquid mixtures with respect to vapor-liquid ones, **plate efficiencies are much lower** (or HTU values are much higher) for solvent extraction operations than for distillation, absorption and stripping.
- ◆ Therefore solvent extraction is practically effective for systems with very high selectivity only.

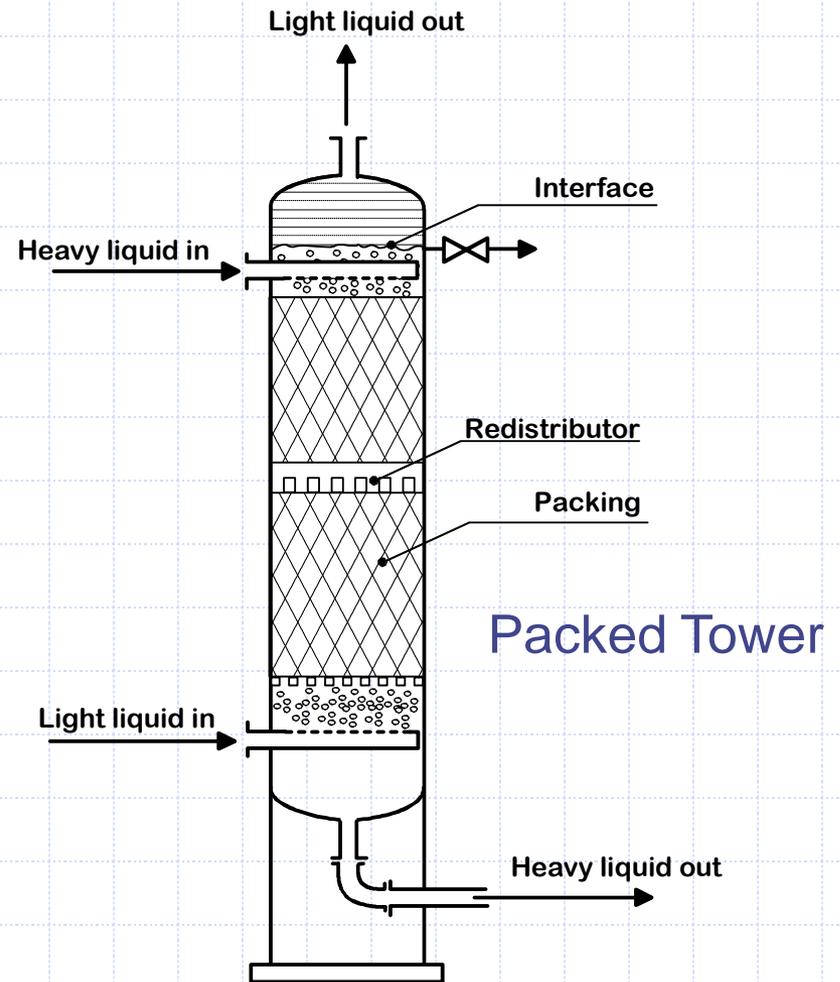
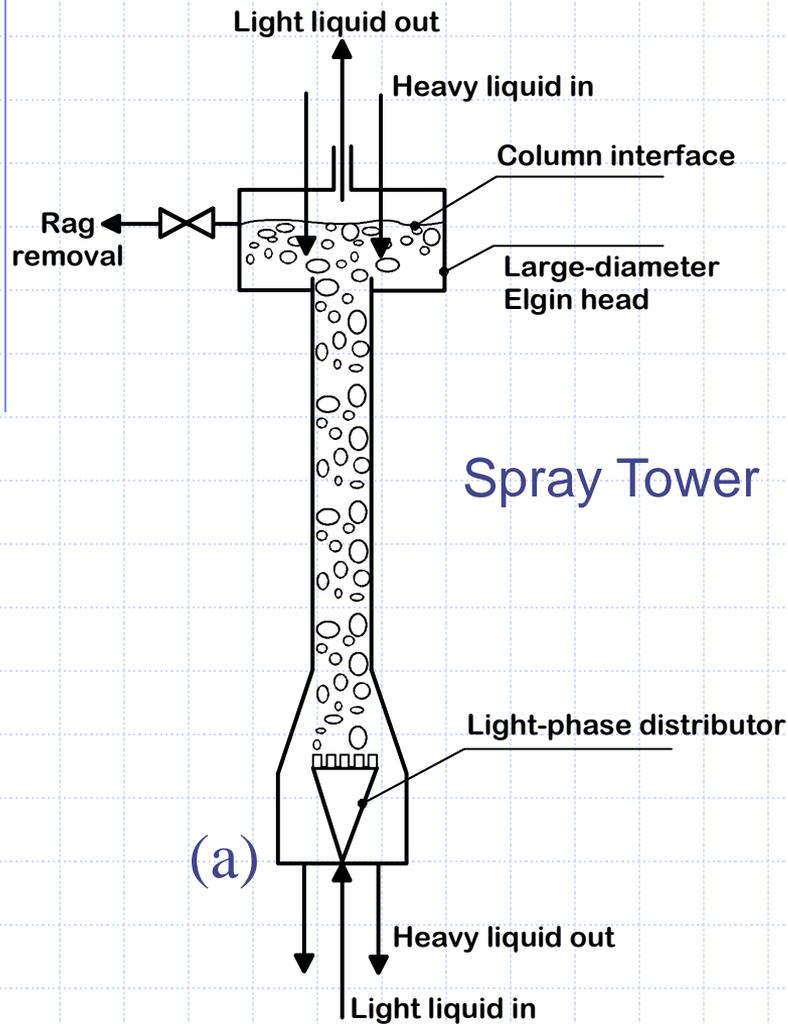


Extraction Equipment Selection

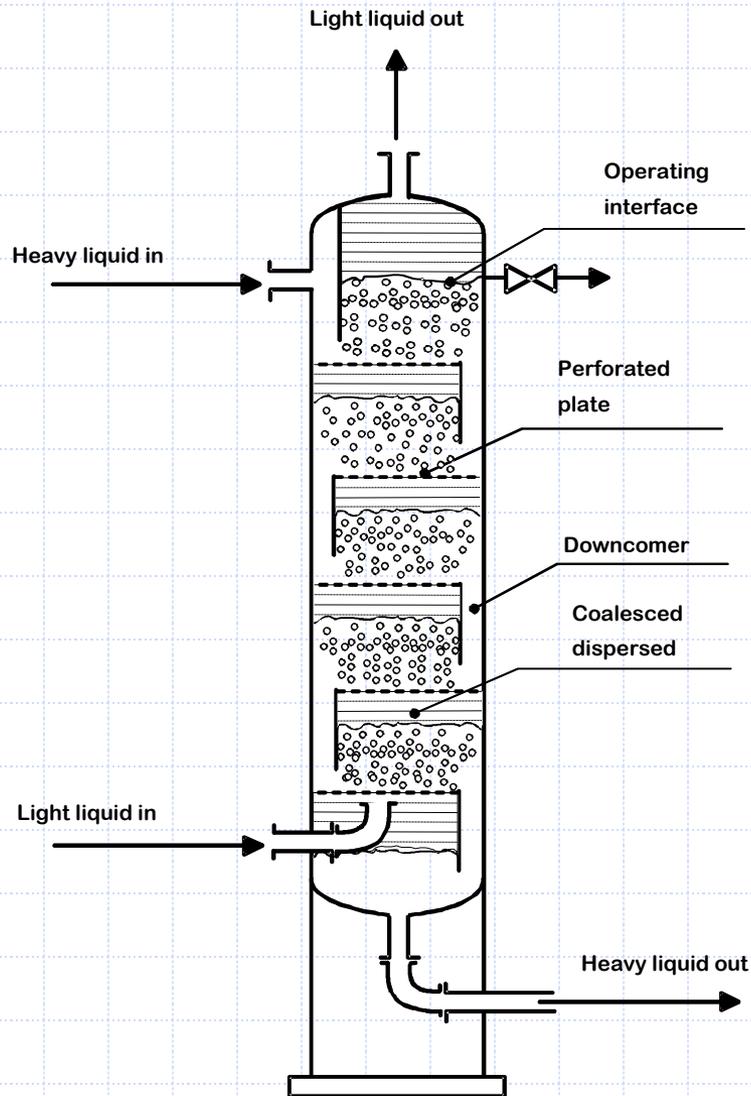
◆ Depends on:

- solvent recovery economics
- viscosities, interfacial tension, solids
- product/solvent value
- flowrates
- risk assessment
- operation experience

Static Columns



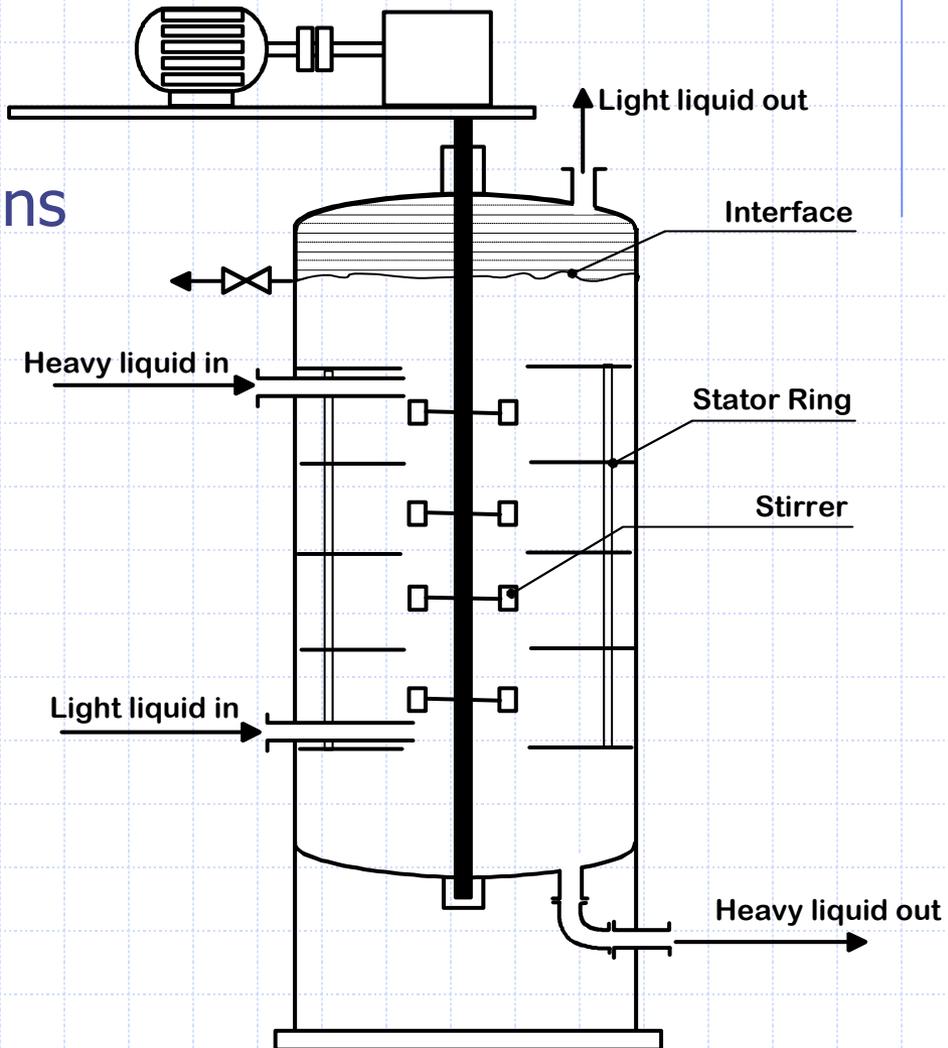
Static Columns



Sieve Tray

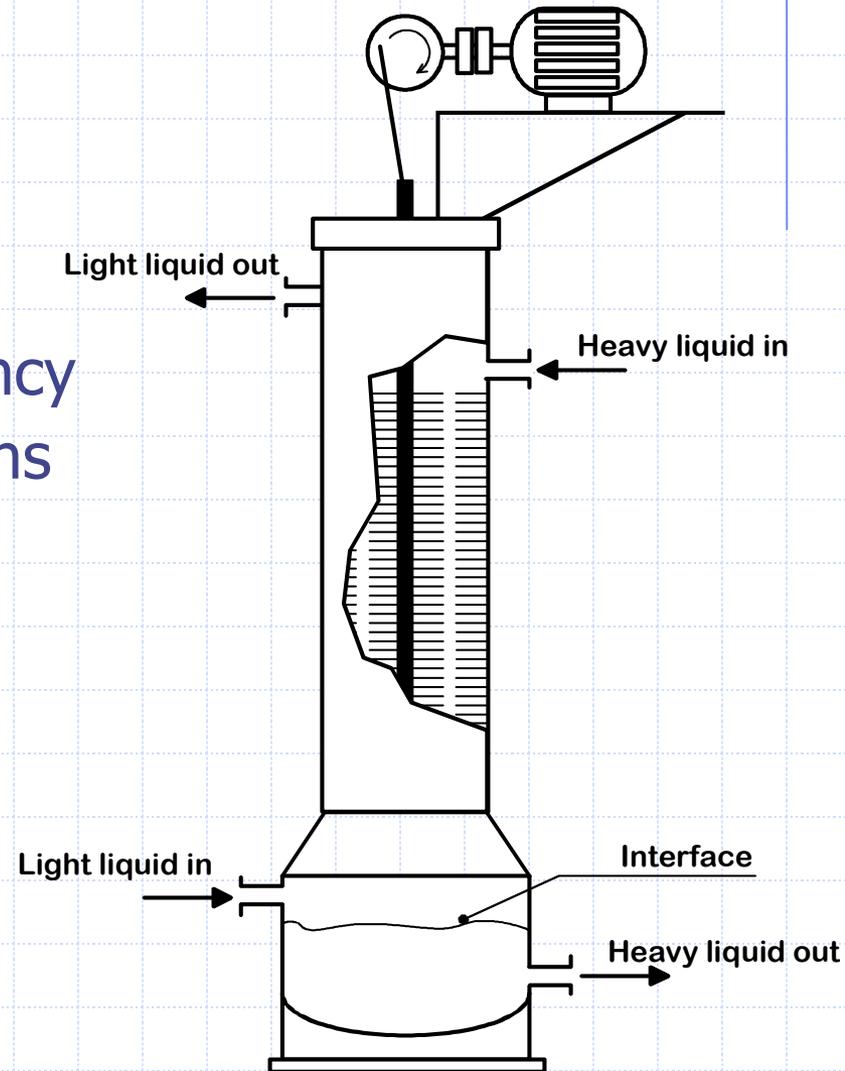
Oldshue-Rushston Column

- ◆ Develop in 1950's
- ◆ Many commercial installations
- ◆ Solids handling
- ◆ Viscosities to 500 cP
- ◆ Differential contactor



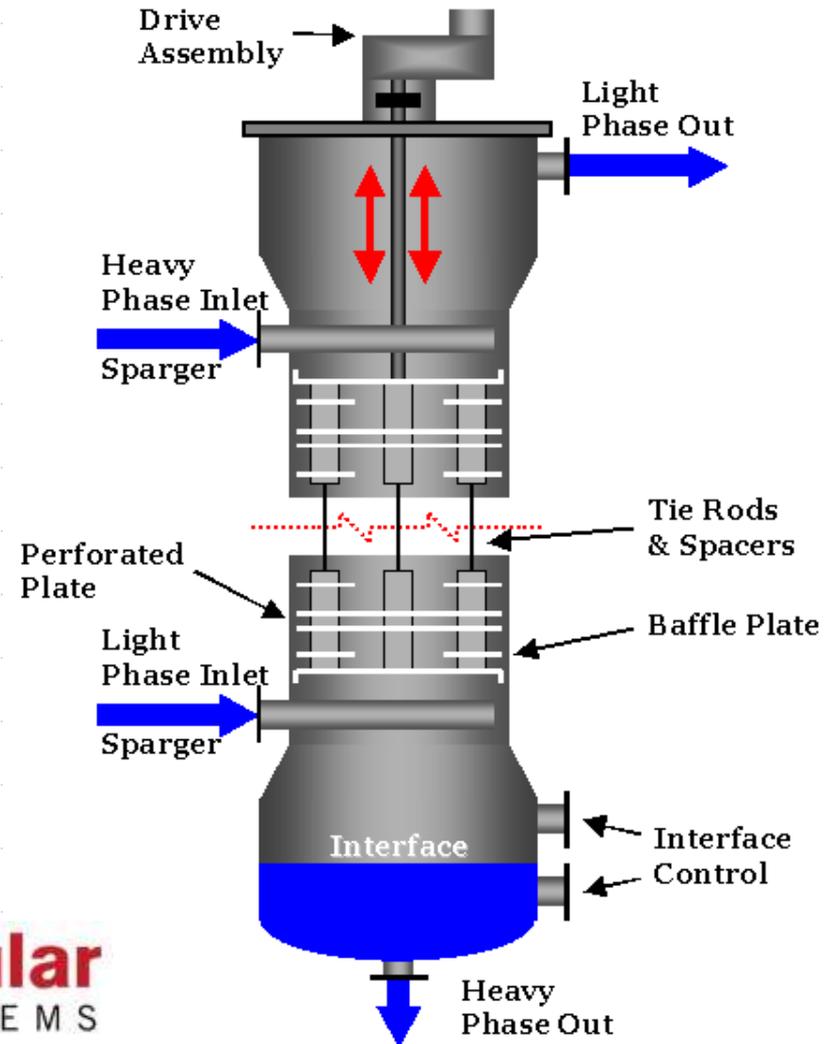
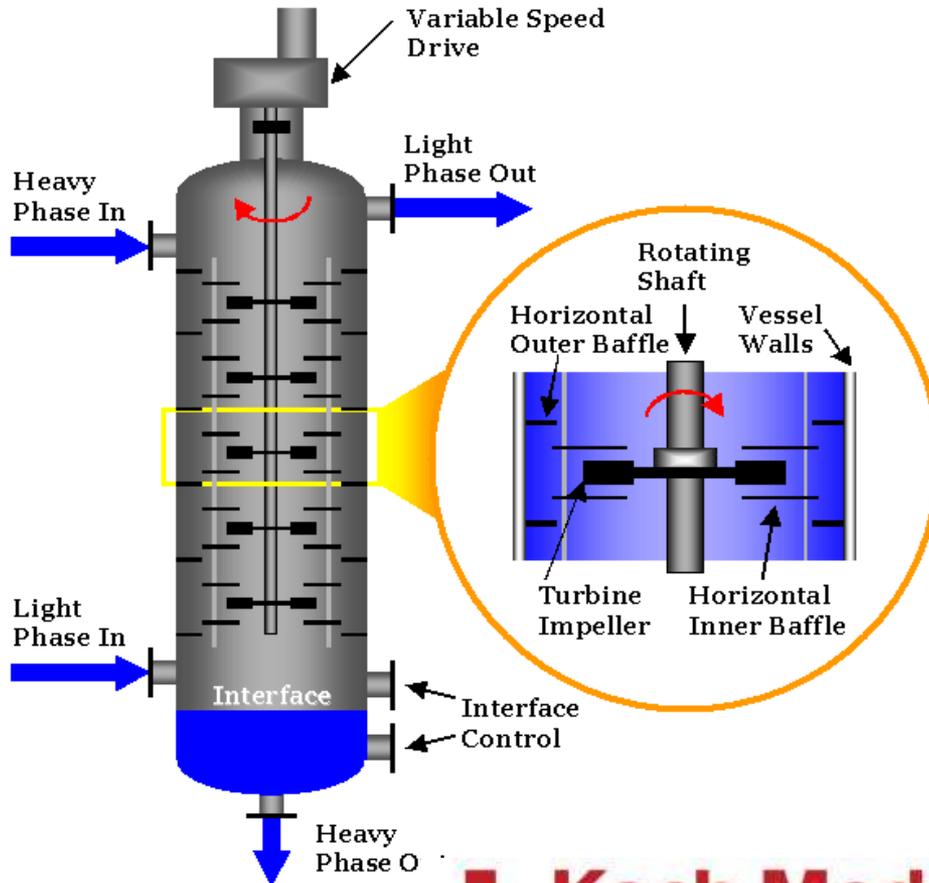
Reciprocating Plate Extractor (Karr)

- ◆ Developed in 1959
- ◆ Many commercial installations
- ◆ V. High Volumetric Efficiency
- ◆ Vary tray amplitude and frequency
- ◆ Caution at low interfacial tensions
- ◆ Tray movement can clean walls
- ◆ Differential contactor
- ◆ Scale-up to the 0.38 power on diameter
- ◆ Other variations (e.g. VPE)



Rotating and oscillating columns

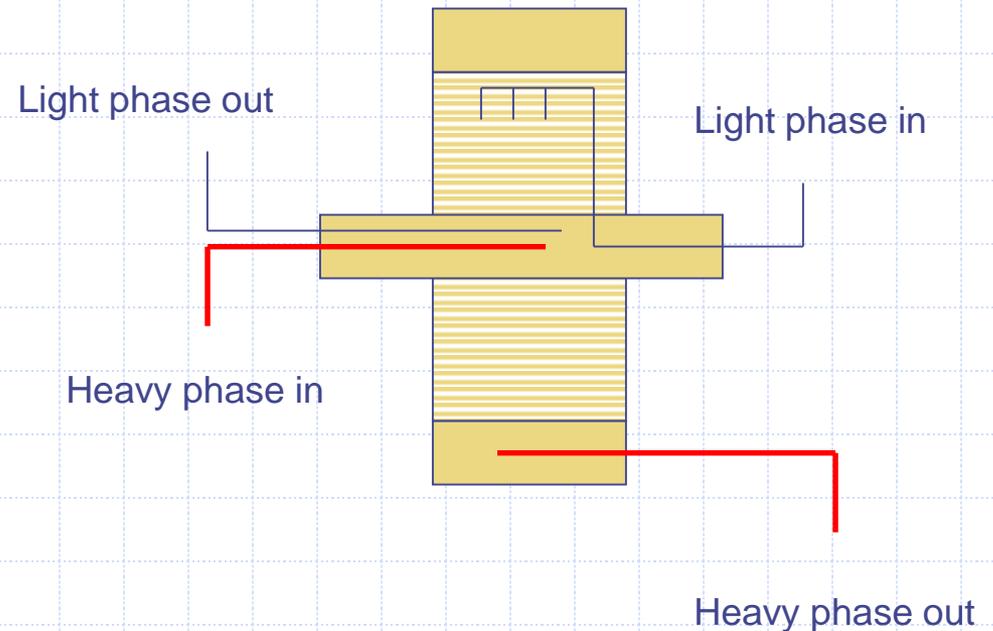
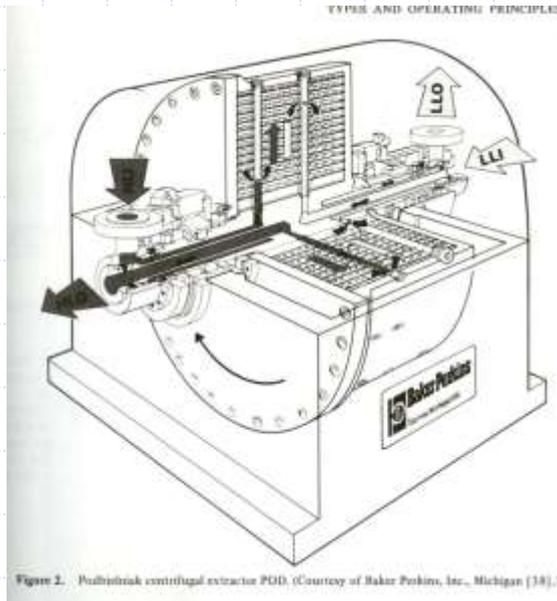
Columns



 **Koch Modular**
PROCESS SYSTEMS

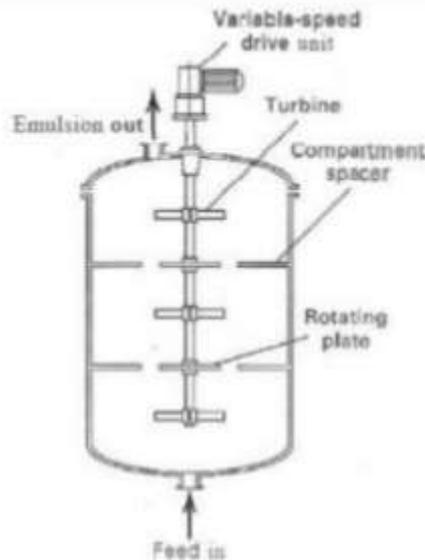
Podbielniak

- ◆ Horizontal centrifugal extractor
- ◆ High efficiency
- ◆ Short residence time
- ◆ Minimum inventory

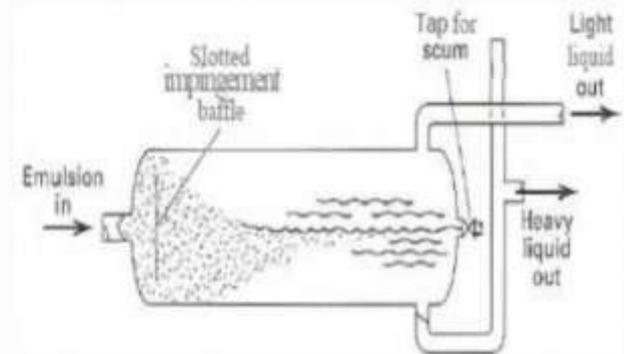


Mixer-Settler

- ◆ A multi-stage mixer-settler system can be realized by coupling a number of mixers and settlers in series.
 - A mixer is a simple tank, with suitable devices to promote mass transfer.
 - A settler is a horizontal vessel with internal baffles suitably arranged so as to decant two immiscible liquid phases thanks to their different density (density difference must be at least 50 kg/m^3)



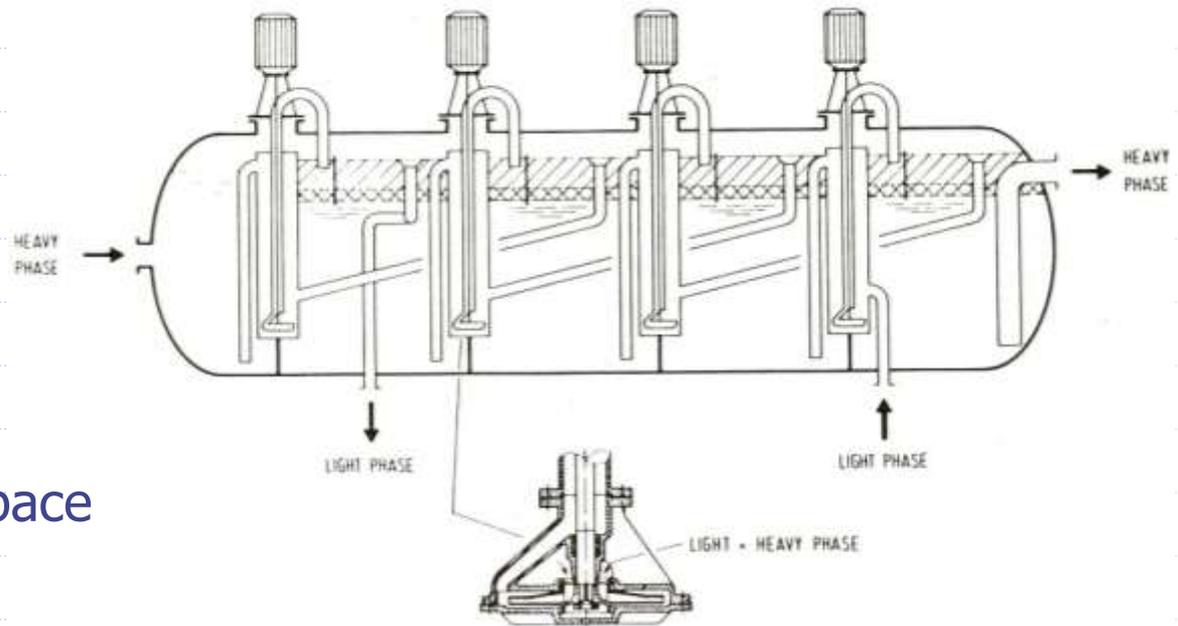
Mixing vessel with variable-speed turbine agitator



Horizontal gravity-settling vessel

Mixer-Settler

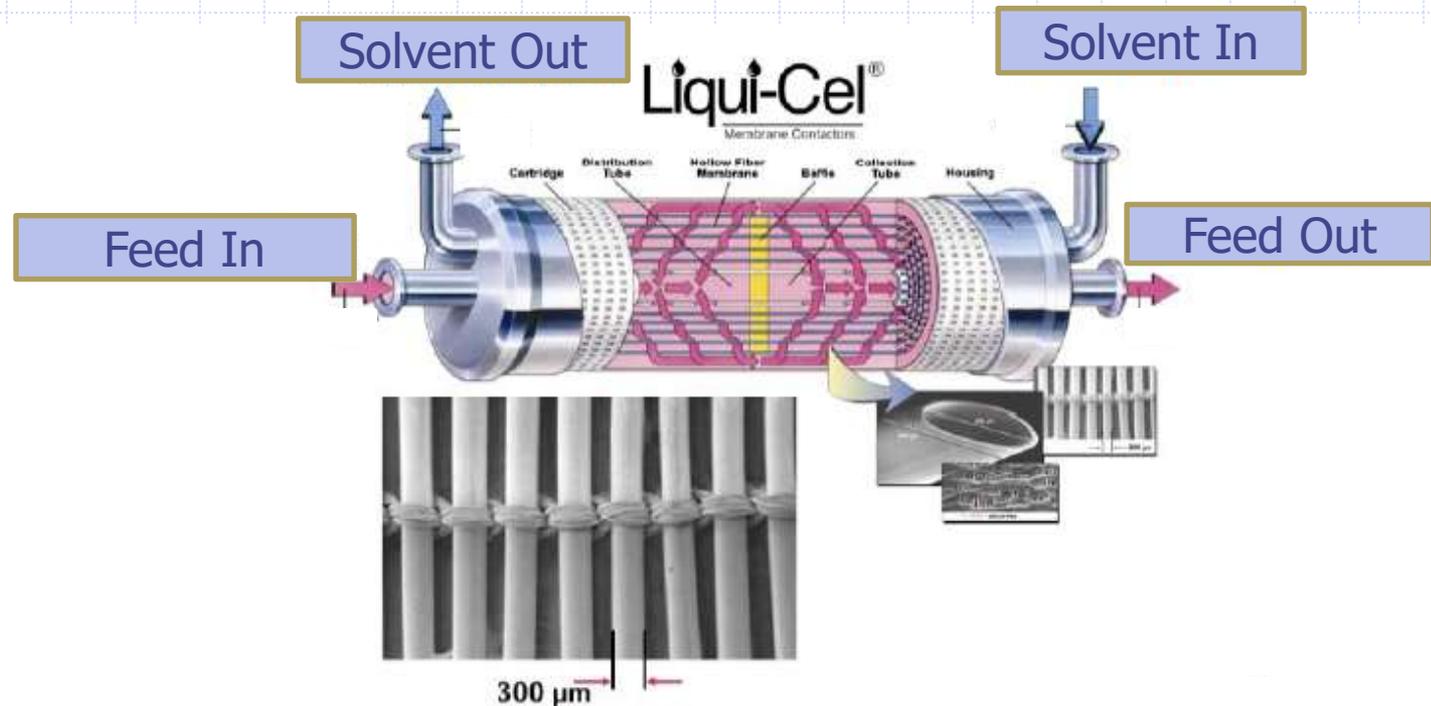
- ◆ Wide range of designs
- ◆ Handle wide range of flow ratios
- ◆ Easy start-up
- ◆ Easy to clean/inspect
- ◆ Batch operations
- ◆ Larger equipment
- ◆ Handles solids
- ◆ Low headroom
- ◆ Occupy much floor space
- ◆ Can add stages
- ◆ Interstage pumping often required
- ◆ High solvent inventory



LURGI multistage extractor with internal vertical inverted impeller mixing pumps

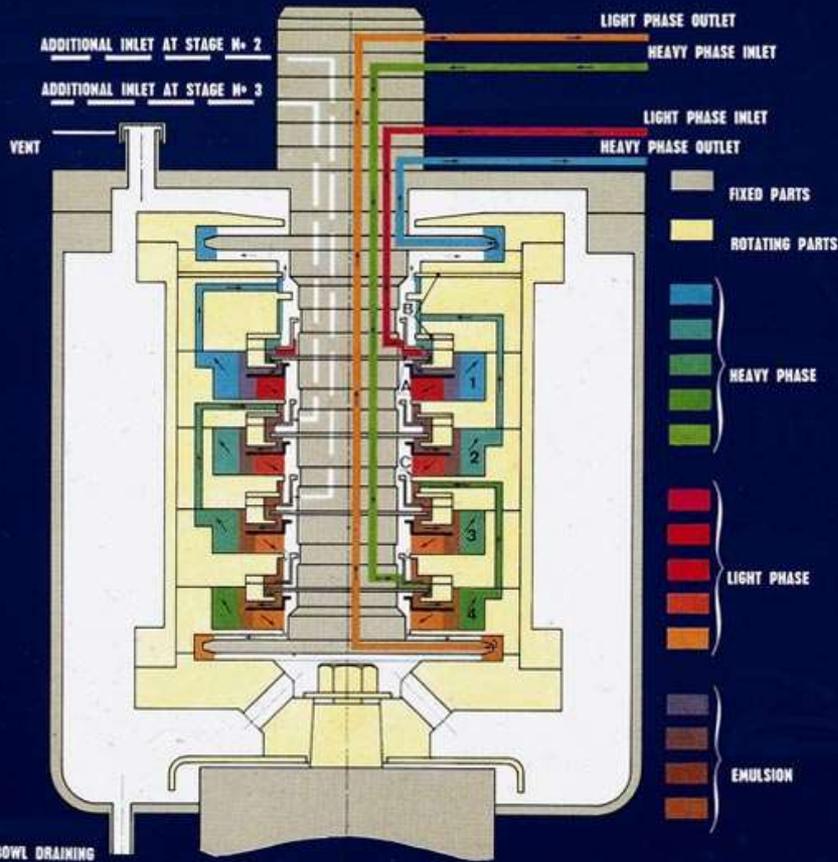
Hollow Fiber Extractor

- ◆ Developed in 1980s - Modified in 1990s
- ◆ Stage contactor
- ◆ Low organic solvent to aqueous feed ratios
- ◆ Few commercial extraction applications
- ◆ Many commercial gas/liquid applications

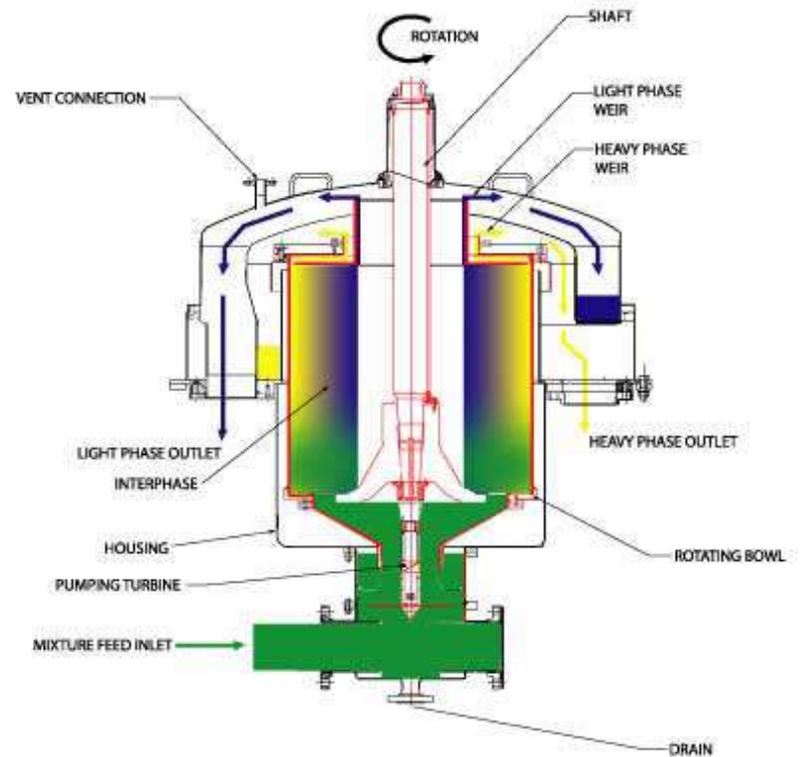


Centrifugal extractors

CROSS SECTION SKETCH 4 STAGE CENTRIFUGAL EXTRACTOR



Rousselet-Robatel Model BXP Centrifugal Separator



LL extraction with Aspen+: Extract

- ◆ Water has a high latent heat (heat of vaporization) compared to many other components.
- ◆ For the separation of a water-acetone mixture (50 wt-% each), it may be more energy efficient to use extraction instead of direct distillation.
 - Feed is at 25°C, 1 bar, 50 kg/hr water and 50 kg/hr acetone
 - Use 3 methyl hexane as solvent: 150 kg/hr at 30°C, 1 bar
 - EXTRACT: N=8, P=1 bar, T=25°C
 - Use Uniquac – RK thermodynamics
- ◆ Solution
 - Plot the ternary LLE diagram with miscibility gap and tie lines
 - Verify the mass flows (kg/hr) in the raffinate and extract.
 - Check that mass fraction of acetone in the raffinate is less than 0.0001
 - Check that mass fraction of water in the extract is less than 0.002.

LL extraction with Aspen+: Extract

◆ Components

Component ID	Type	Component name	Alias
WATER	Conventional	WATER	H2O
ACETONE	Conventional	ACETONE	C3H6O-1
3-METC6	Conventional	3-METHYLHEXANE	C7H16-3

◆ Method

Global | Flowsheet Sections | Referenced | Comments

Property methods & options

Method filter: **CHEMICAL**

Base method: **UNIQ-RK**

Henry components: []

Petroleum calculation options

Free-water method: **STEAM-TA**

Water solubility: **3**

Electrolyte calculation options

Chemistry ID: []

Method name: **UNIQ-RK**

Modify

Vapor EOS: []

Data set: []

Liquid gamma: []

Data set: []

Liquid molar enthalpy: []

◆ Feed

Solvent

Mixed | CI Solid | NC Solid | Flash Options | EO Options | Costing | Comments

Specifications

Flash Type: **Temperature** | **Pressure**

State variables

Temperature: **25 C**

Pressure: **1 bar**

Vapor fraction: []

Total flow basis: **Mass**

Total flow rate: [] **kg/hr**

Solvent: []

Composition

Mass-Flow | **kg/hr**

Component	Value
WATER	50
ACETONE	50
3-METC6	

Mixed | CI Solid | NC Solid | Flash Options | EO Options | Costing | Comments

Specifications

Flash Type: **Temperature** | **Pressure**

State variables

Temperature: **30 C**

Pressure: **1 bar**

Vapor fraction: []

Total flow basis: **Mass**

Total flow rate: [] **kg/hr**

Solvent: []

Reference Temperature: []

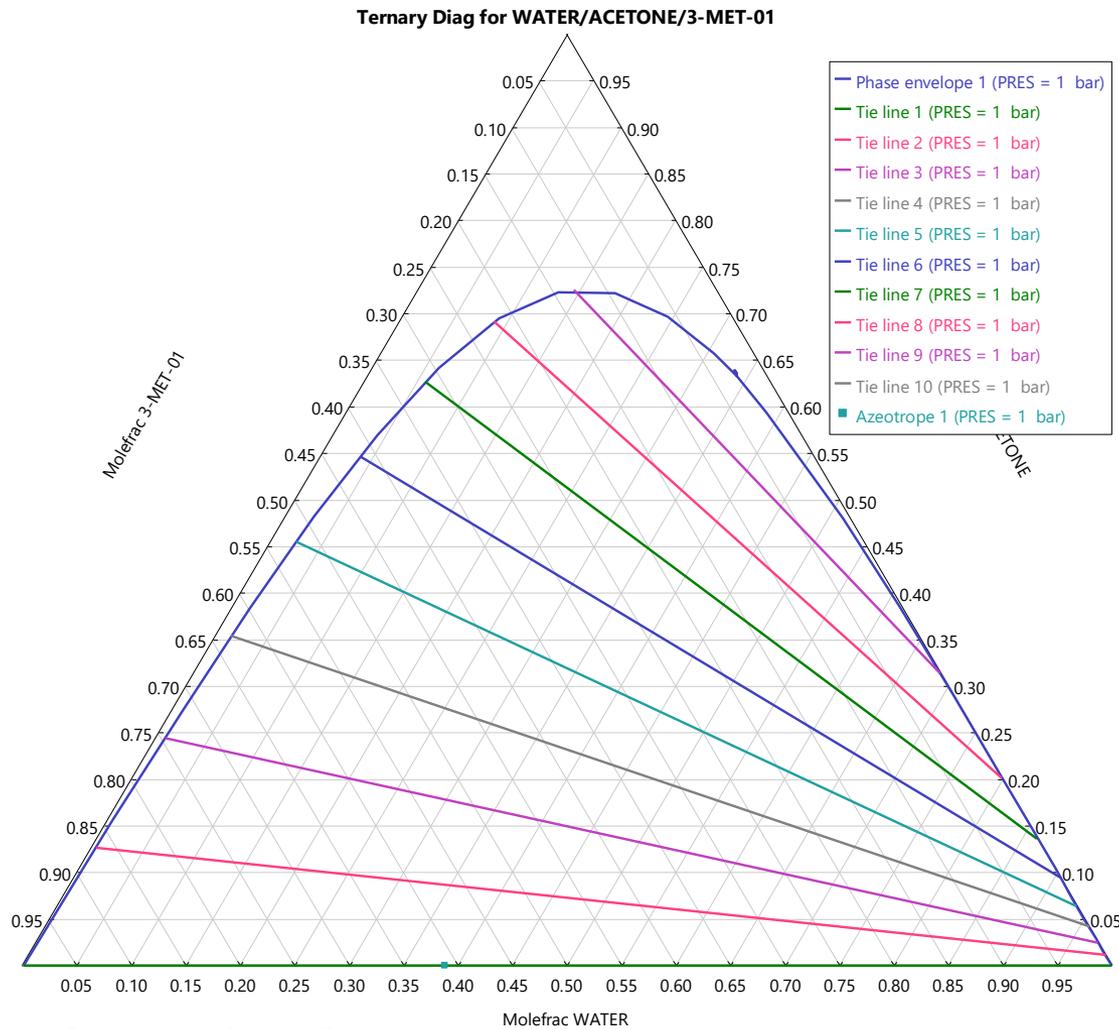
Composition

Mass-Flow | **kg/hr**

Component	Value
WATER	
ACETONE	
3-METC6	150

LL extraction with Aspen+: Extract

Ternary diagram at 1 bar



LL extraction with Aspen+: Extract

Extract

The image shows several Aspen+ configuration windows for an Extract process:

- Configuration:** Number of stages is set to 8. Thermal options include Adiabatic, Specify temperature profile, and Specify heat duty profile.
- Pressure profile:** Shows a single stage with a pressure of 1 atm.
- Estimates:** Temperature estimates for Stage 1 are shown as 25 C. A 'Generate Estimates...' button is visible.
- Outside Loop:** Convergence method is set to Broyden, with 200 maximum iterations and an error tolerance of 1e-05.
- Streams:** Shows the composition of the 1st and 2nd liquid phases. The 1st liquid phase contains ACETONE and 3-METC6. The 2nd liquid phase contains WATER and 3-METC6.

Stream Results

	Units	FEED	SOLVENT	EXTRACT	RAFFIN
Mass Enthalpy	kcal/kg	-2420.27	-537.074	-670.32	-3785.13
Molar Entropy	cal/mol-K	-48.4508	-179.621	-142.026	-38.741
Mass Entropy	cal/gm-K	-1.76182	-1.79255	-1.68177	-2.15033
Molar Density	kmol/cum	31.854	6.87789	8.76877	54.9623
Mass Density	kg/cum	876.001	689.193	740.526	990.218
Enthalpy Flow	Gcal/hr	-0.242027	-0.0805611	-0.134222	-0.188367
Average MW		27.5005	100.204	84.4505	18.0163
+ Mole Flows	kmol/hr	3.6363	1.49695	2.37104	2.76221
+ Mole Fractions					
+ Mass Flows	kg/hr	100	150	200.235	49.7649
- Mass Fractions					
WATER		0.5	0	0.0011946	0.999918
ACETONE		0.5	0	0.249687	7.63842e-05
3-MET-01		0	1	0.749118	5.49238e-06
Volume Flow	cum/hr	0.114155	0.217646	0.270396	0.0502565