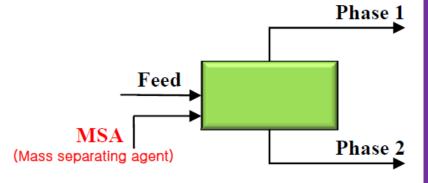
# **Extraction**



**Principal references:** Chapter 12 in C.J. Geankoplis book and Chapter 8 in Henley, Seader & Roper book

- •Liquid-Liquid Extraction (LLE)
  - •(solvent extraction)



**Based on phase-addition** 

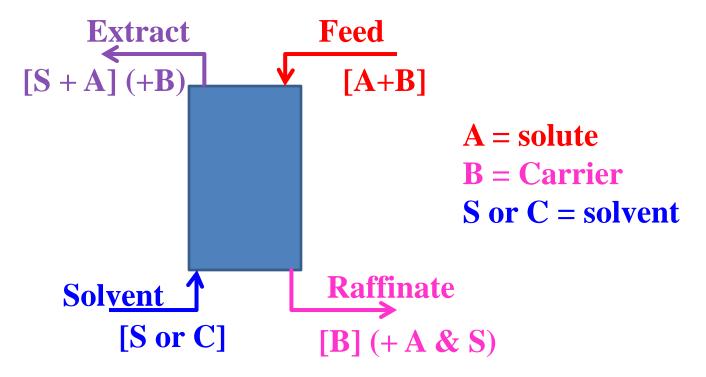
- Pioneered during 1940's (uranium purification)
- Alternative to distillation, absorption/stripping
  - Energy savings
  - Sometimes easier separation
  - Lower temperatures
- Usually two distinct phases formed:
  - light phase
  - heavy phase

#### Where LLE is used?

- Bioseparations.
- Nuclear (uranium recovery).
- Mining: nickel/cobalt; copper/iron.
- Perfumes, fragrances and essential oils.
- Fine and specialty chemicals.
- Oil sands: extract bitumen away from water.

#### Why LLE?

- 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.



let: x = massfraction solute in raffinate phase y = massfraction solute in extractphasey\*=in equilibrium with associated x

#### **Main objectives of LLE:**

- High recovery of solute overall (low  $x_R$  and high  $y_E$ ).
- Concentrated solute in extract (high y<sub>E</sub>)

- > Solute: species to be recovered from the feed
- > Feed: "feed solvent": "carrier" of solute.
- > Solvent: MSA (by convention: the "added" liquid).
- **Extract:** solvent (not solute) mostly present in this layer.

 $y_{E,A}$  or  $y_A$  = concentration of A, the solute, in extract.

We aim for the solute (A) to be mostly in the extract stream.

Raffinate: residual solute in this layer.

 $x_{R,A}$  or  $x_A$ = concentration of A, the solute, in raffinite.

**Distribution coefficient**: quantitative measure of how the solute partitions itself at equilibrium:  $K_A = y_A/x_A$ 

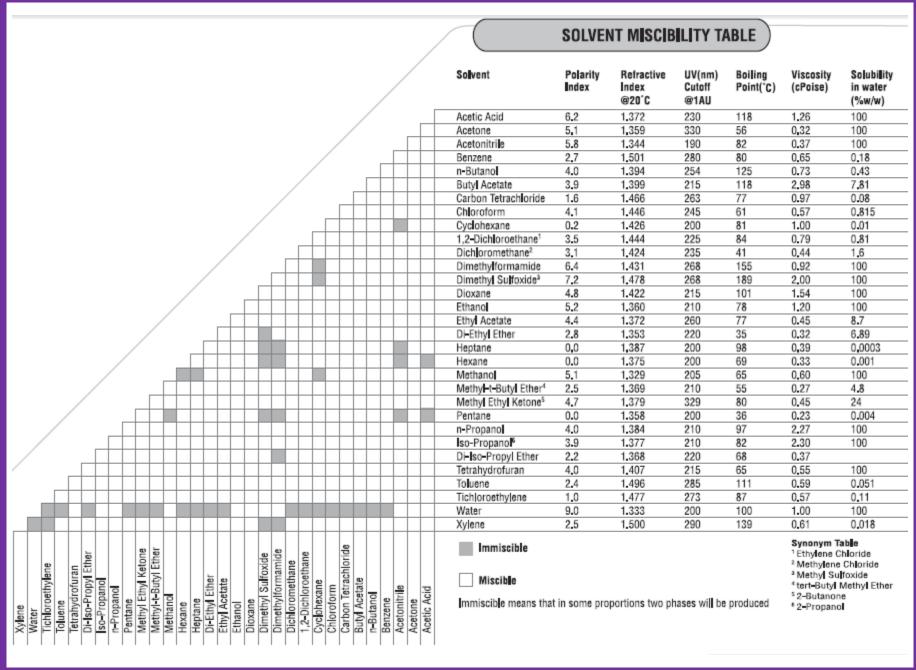
- Measure affinity of solute
- From thermodynamic view:

$$K_A = (\mu_A^R - \mu_A^E)/(RT)$$

 $\triangleright$  **Relative selectivity,**  $\beta$ , of solute with respect to the carrier:

$$\beta = \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B}$$

- Extraction unit (extractor) could be:
  - Column in stages or packing.
  - Column with moving internals.
  - single stage mixer/settler.
  - Equilibrium stage(s).
- > LLE is usually coupled with another separation technique.
- > Solvent miscibility is one of the main factors that play key role in LLE process.



#### Three major steps required in LLE:

#### 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

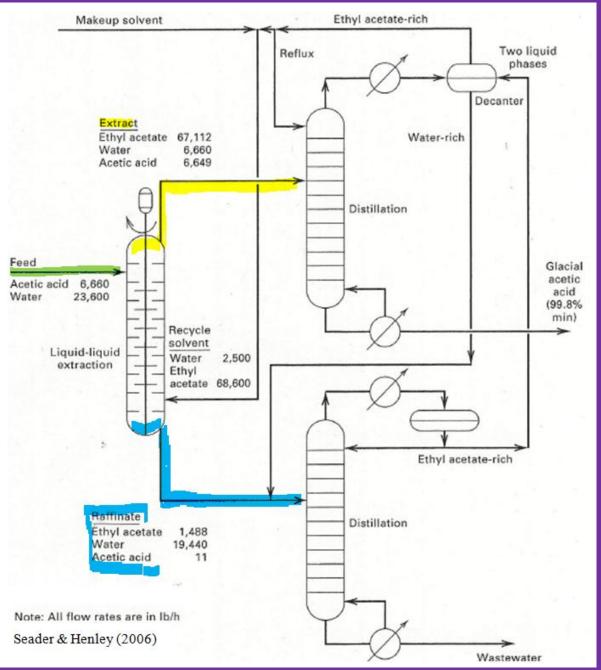
#### 2. Phase separation:

- reverse of above mixing step
- drops come together and coalesce
- relies on density difference

#### 3. Collection of phases leaving the unit

split the raffinate from the extract

# **Typical LLE Process**



# **Examples of Industrial LLE Processes**

Table 8.1 Representative Industrial Liquid–Liquid Extraction Processes

Solute	Carrier	Solvent		
Acetic acid	Water	Ethyl acetate		
Acetic acid	Water	Isopropyl acetate		
Aconitic acid	Molasses	Methyl ethyl ketone		
Ammonia	Butenes	Water		
Aromatics	Paraffins	Diethylene glycol		
Aromatics	Paraffins	Furfural		
Aromatics	Kerosene	Sulfur dioxide		
Aromatics	Paraffins	Sulfur dioxide Furfural		
Asphaltenes	Hydrocarbon oil			
Benzoic acid	Water	Benzene		
Butadiene	1-Butene	aq. Cuprammonium acetate		
Ethylene cyanohydrin	Methyl ethyl ketone	Brine liquor		
Fatty acids	Oil	Propane		
Formaldehyde	Water	Isopropyl ether		
Formic acid	acid Water Tetrahydr			

# **Examples of Industrial LLE Processes**

Solute	Carrier	Solvent		
Glycerol	Water	High alcohols		
Hydrogen peroxide	Anthrahydroquinone	Water		
Methyl ethyl ketone	Water	Trichloroethane		
Methyl borate	Methanol	Hydrocarbons		
Naphthenes	Distillate oil	Nitrobenzene		
Naphthenes/ aromatics	Distillate oil	Phenol		
Phenol	Water	Benzene		
Phenol	Water	Chlorobenzene		
Penicillin	Broth	Butyl acetate		
Sodium chloride	aq. Sodium hydroxide	Ammonia		
Vanilla	Oxidized liquors	Toluene		
Vitamin A	Fish-liver oil	Propane		
Vitamin E	Vegetable oil	Propane		
Water	Methyl ethyl ketone			

#### Selecting a solvent for LLE Processes

■ 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.

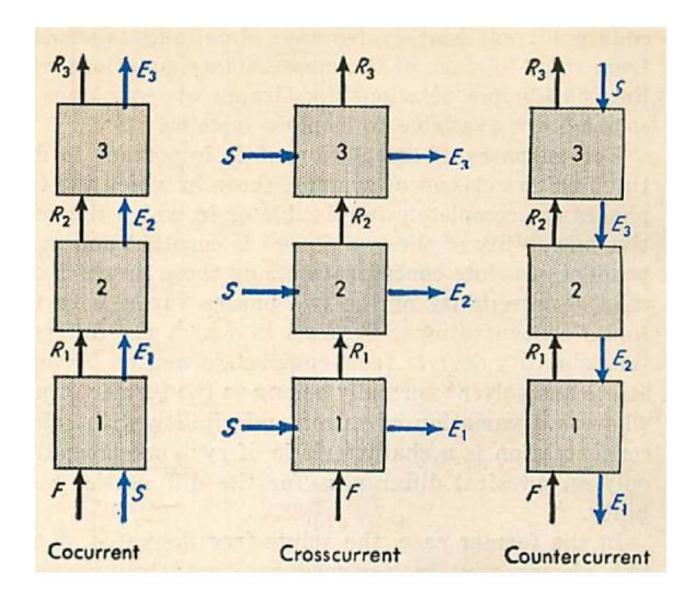
#### ■ The ideal solvent has:

- 1. A high selectivity for the solute relative to the carrier.
- 2. A high capacity for dissolving the solute, so as to minimize the solvent-to-feed ratio.
- 3. A minimal solubility in the carrier.
- 4. A volatility sufficiently different from the solute:
  - recovery of the solvent can be achieved by distillation.
  - the vapor pressure should not be so high that a high extractor pressure is needed.
  - the vapor pressure should not be so low that a high temperature is needed if the solvent is recovered by distillation.

## **Selecting a solvent for LLE Processes**

- 5. Stability to maximize the solvent life and minimize the solvent make-up requirement.
- 6. Inertness to permit use of common materials of construction.
- 7. A low viscosity to promote phase separation, minimize pressure drop, and provide a high solute mass transfer rate.
- 8. Nontoxic and nonflammable characteristics.
- 9. Availability at a relatively low cost.
- 10. Reasonable surface tension: easy to disperse and coalesce.
- 11. A large difference in density relative to the carrier to achieve a high capacity in the extractor.
- 12. Compatibility with the solute and carrier to avoid contamination.
- 13. No tendency to form a stable rag or scum (foam) layer at the phase interface
- 14. Desirable wetting characteristics with respect to extractor internals

# **Modes LLE Operations**



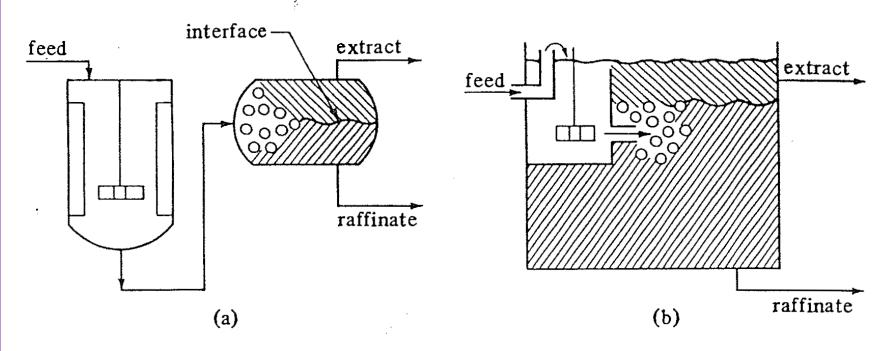


FIGURE 12.6-1. Typical-mixer-settlers for extraction: (a) separate mixer-settler, (b) combined mixer-settler.

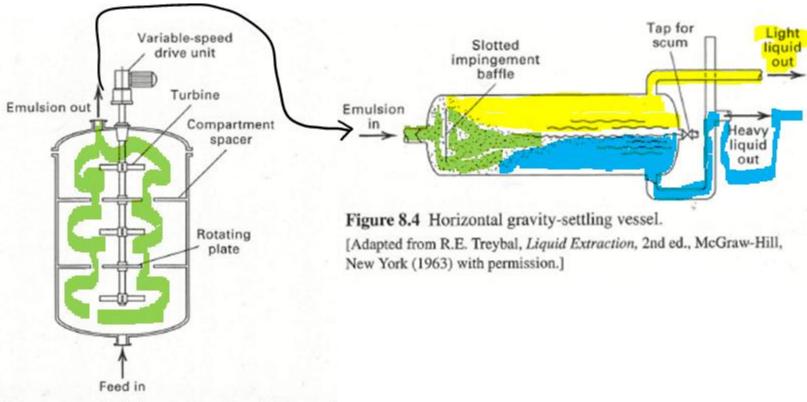


Figure 8.2 Compartmented mixing vessel with variable-speed turbine agitators.

[Adapted from R.E. Treybal, Mass Transfer, 3rd ed., McGraw-Hill, New York (1980).] Seader & Henley (2006)

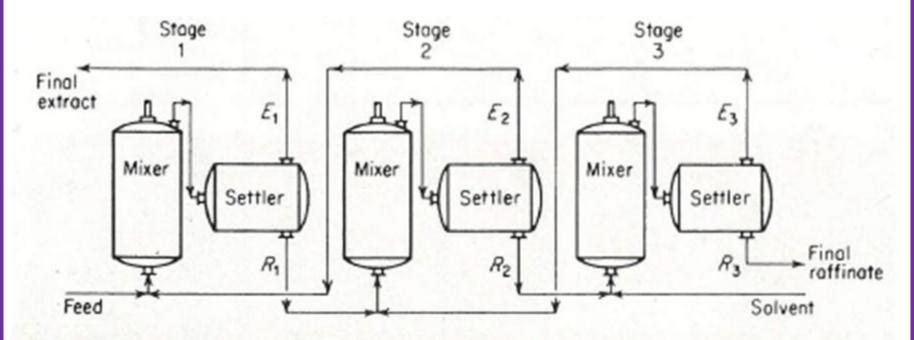
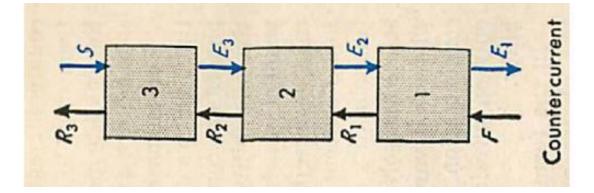
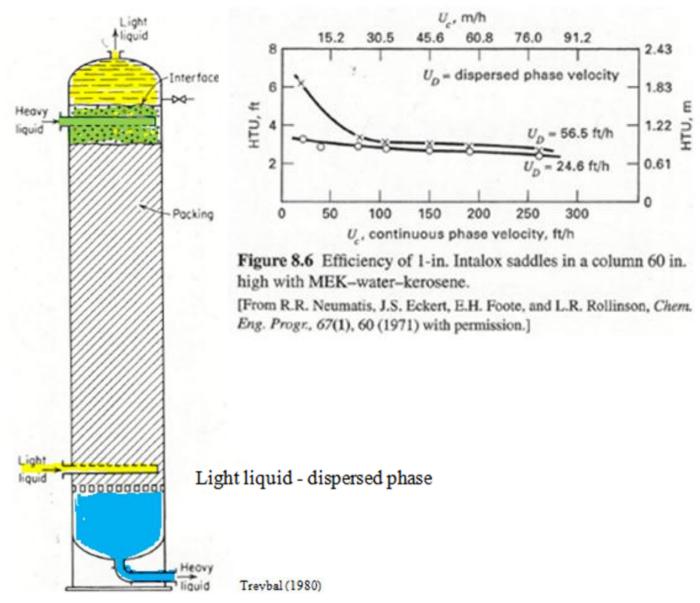


Figure 10.41 Flowsheet of three-stage countercurrent mixer-settler extraction cascade.

Treybal (1980)



Packed-bed Column



**Some LLE Equipments** Light Spray Columns: liquid Light liquid Heavy Heavy liquid Light Light liquid liquid Heavy Heavy liquid liquid (a) (b)

Figure 8.5 Spray columns: (a) light liquid dispersed, heavy liquid continuous. Seader & Henley (2006)

Sieve-tray Extraction Column: light phase dispersed

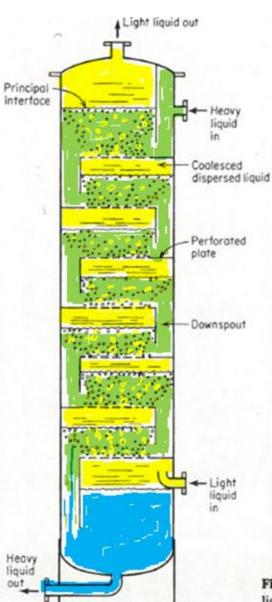
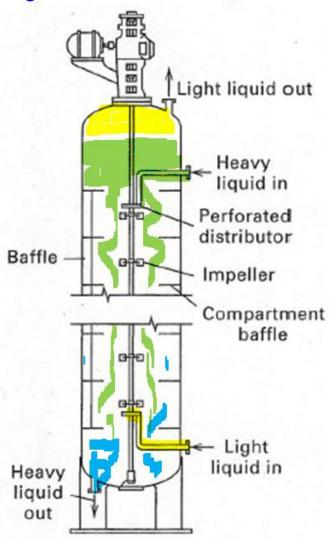
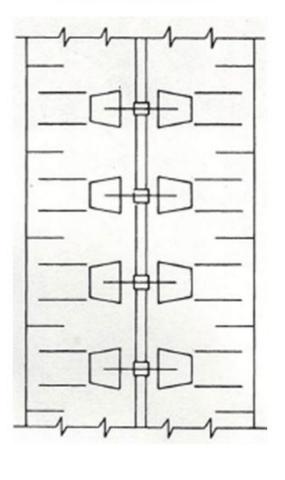


Figure 10.44 Sieve-tray extraction tower, arranged for light liquid dispersed. Treybal (1980)

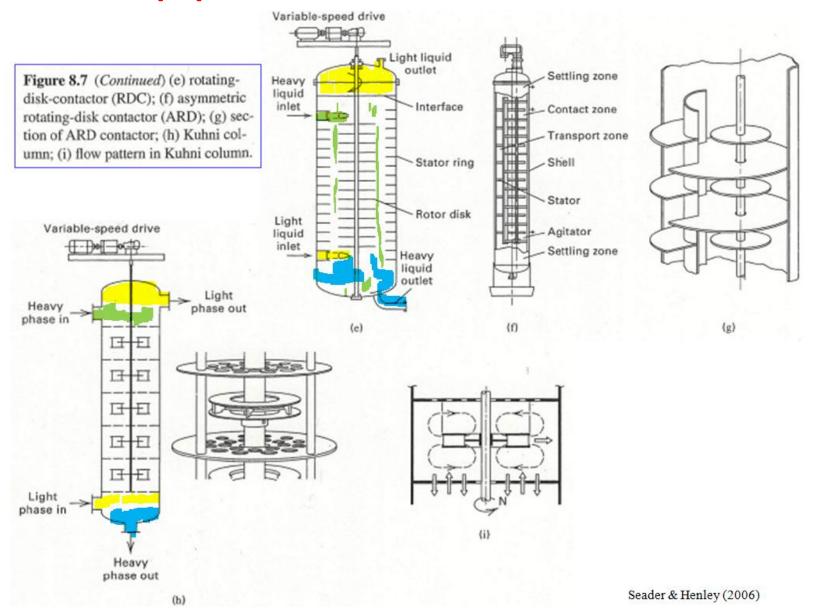
Oldshue-Rushton (Mixco Lightnin CMContactor) column



#### Scheibel column



Seader & Henley (2006)



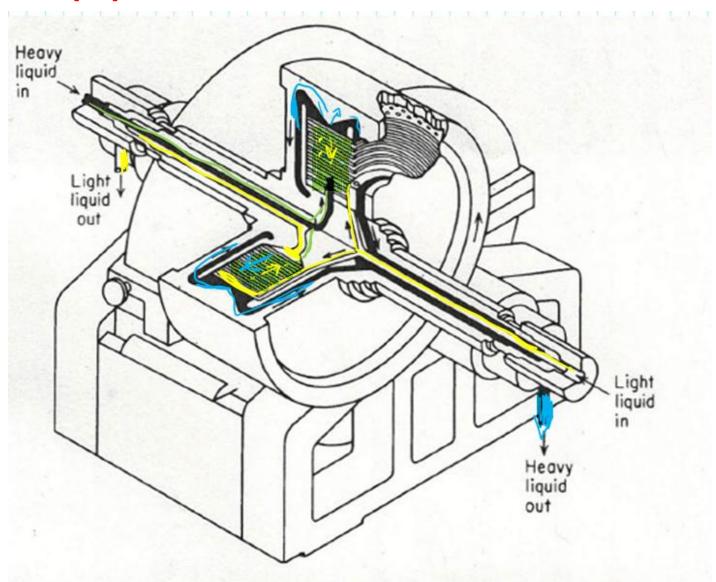


Figure 10.56 Podbielniak centrifugal extractor (schematic). (Podbielniak, Inc.)

Table 8.3 Advantages and Disadvantages of Different Extraction Equipment

Class of Equipment	Advantages	Disadvantages		
Mixer-settlers	Good contacting	Large holdup		
	Handles wide flow ratio	High power costs		
	Low headroom	High investment		
	High efficiency	Large floor space		
	Many stages available Reliable scale-up	Interstage pumping may be required		
Continuous, counterflow contactors (no mechanical drive)	Low initial cost Low operating cost	Limited throughput with small density difference		
	Simplest construction	Cannot handle high flow ratio		
		High headroom		
		Sometimes low efficiency		
		Difficult scale-up		
Continuous, counterflow contactors (mechanical	Good dispersion Reasonable cost	Limited throughput with small density difference		
agitation)	Many stages possible	Cannot handle emulsifying systems		
	Relatively easy scale-up	Cannot handle high flow ratio		
Centrifugal extractors	Handles low-density	High initial costs		
	difference between phases	High operating cost		
	Low holdup volume	High maintenance cost		
	Short holdup time	Limited number of stages		
	Low space requirements	in single unit		
	Small inventory of solvent			

Table 8.2 Maximum Size and Loading for Commercial Liquid–Liquid Extraction Columns

Column Type	Approximate Maximum Liquid Throughout, m <sup>3</sup> /m <sup>2</sup> -h	Maximum Column Diameter, m	
Lurgi tower	30	8.0	
Pulsed packed	40	3.0	
Pulsed sieve tray	60	3.0	
Scheibel	40	3.0	
RDC	40	8.0	
ARD	25	5.0	
Kuhni	50	3.0	
Karr	100	1.5	
Graesser	<10	7.0	

#### Above data apply to systems of:

- 1. High interfacial surface tension (30 to 40 dyne/cm).
- 2. Viscosity of approximately 1 cP.
- 3. Volumetric phase ratio of 1:1.
- Phase-density difference of approximately 0.6 g/cm<sup>3</sup>.

Liquid-liquid equilibrium in extraction

- **■** Two phases:
  - Extract
  - Raffinate phases
- **Usually three components:** 
  - Solute (A)
  - Carrier (B)
  - Solvent (C or S)

(ternary system)



At certain Temperature and pressure

#### Liquid-liquid equilibrium in extraction

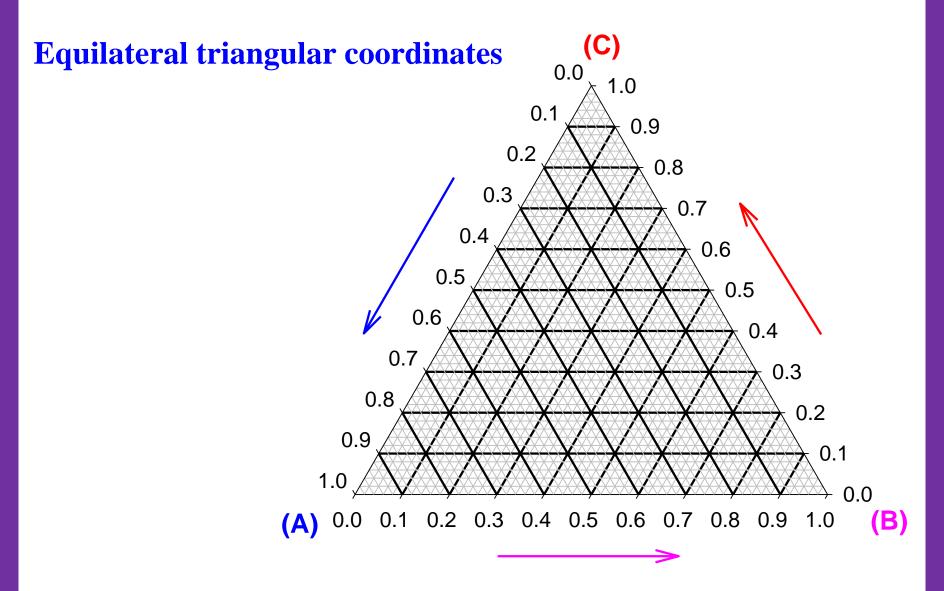
#### Gibbs phase rule:

$$F = 2 - \pi + N$$

where F is the degrees of freedom for nonreacting systems:  $\pi$  is the number of phases, N is the number of chemical species.

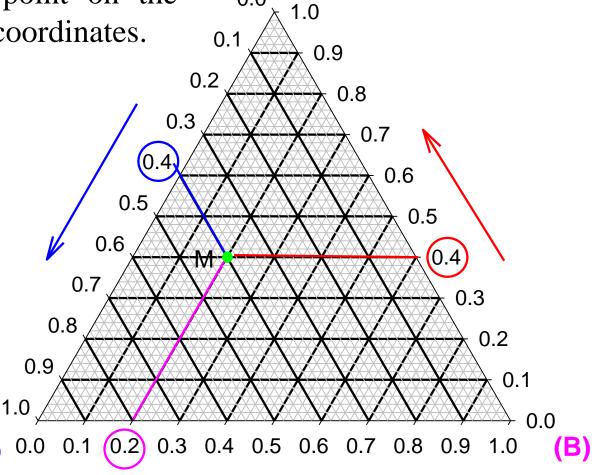
- For LLE:  $F=2-2+3=3 \rightarrow$  three intensive properties can be specified and the others can be determined.
- Usual case: temperature, pressure and one species concentration in either extract or raffinate phase are set. At equilibrium, the other five concentrations can be determined.
- Remember that:

$$x_A + x_B + x_C = 1$$
 (Raffinate phase)  
 $y_A + y_B + y_C = 1$  (Extract phase)



**Example.** The mass composition of ternary mixture is  $x_A=0.4$ ,  $x_B=0.2$ . Locate this point on the equilateral triangular coordinates.

$$x_{c} = 1 - x_{A} - x_{B} = 0.4$$

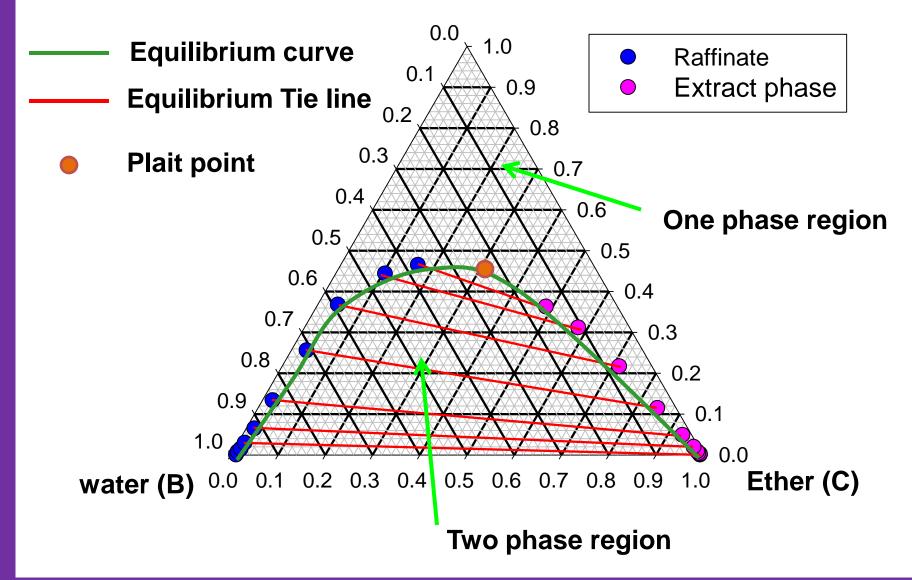


(C)

**Example.** Given liquid-liquid equilibrium data for acetic acid (solute)-water (carrier)- Isopropyl ether (solvent) at 20 °C and 1 atm. Draw the phase diagram on the equilateral triangular coordinates.

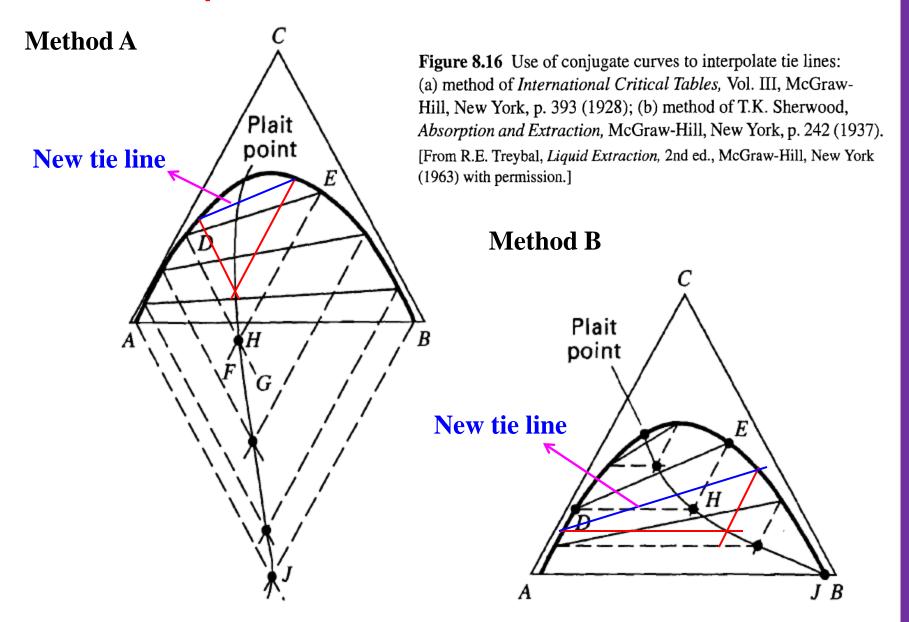
	Mass fraction (x)		Mass fraction (y)			
	water layer			Isopropyl ether layer		
	(Raffinate)			(extract)		
	Acetic	Water	Isopropyl	Acetic	Water	Isopropyl
Run	acid		Ether	acid		Ether
1	0.0000	0.9880	0.0120	0.0000	0.0060	0.9940
2	0.0070	0.9810	0.0120	0.0020	0.0050	0.9930
3	0.0140	0.9710	0.0150	0.0040	0.0070	0.9890
4	0.0290	0.9550	0.0160	0.0080	0.0080	0.9840
5	0.0640	0.9170	0.0190	0.0190	0.0100	0.9710
6	0.1330	0.8440	0.0230	0.0480	0.0190	0.9330
7	0.2550	0.7110	0.0340	0.1140	0.0390	0.8470
8	0.3670	0.5890	0.0440	0.2160	0.0690	0.7150
9	0.4430	0.4510	0.1060	0.3110	0.1080	0.5810
10	0.4640	0.3710	0.1650	0.3620	0.1510	0.4870

# Liquid-Liquid Equilibrium Phase Diagram Acetic Acid (A)

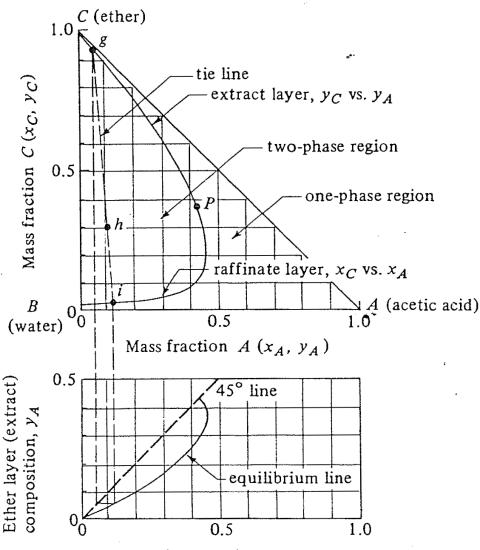


- **Tie line:** line connect the raffinate and extract at equilibrium.
- Tie line located within the two phase region
- Plait point: point on the equilibrium curve at which the compositions in raffinate and extract phases are identical.
- It is evident in the previous figure that the solvent pair B and C are **partially miscible** (two phase region).

#### Tie line interpolation



#### Phase diagram on rectangular coordinates



Water layer (raffinate) composition,  $x_A$ 

FIGURE 12.5-3. Acetic acid (A)—water (B)—isopropyl ether (C) liquid—liquid phase diagram at 293 K (20°C).

#### Common classes of ternary liquid-liquid systems

One immiscible or partially miscible pair:

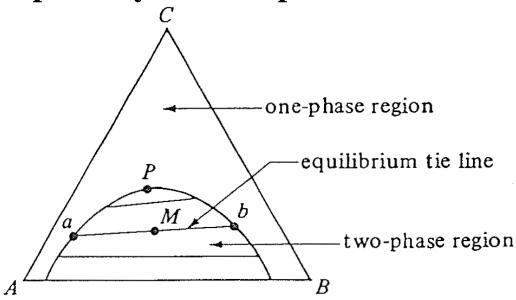


FIGURE 12.5-2. Liquid-liquid phase diagram where components A and B are partially miscible.

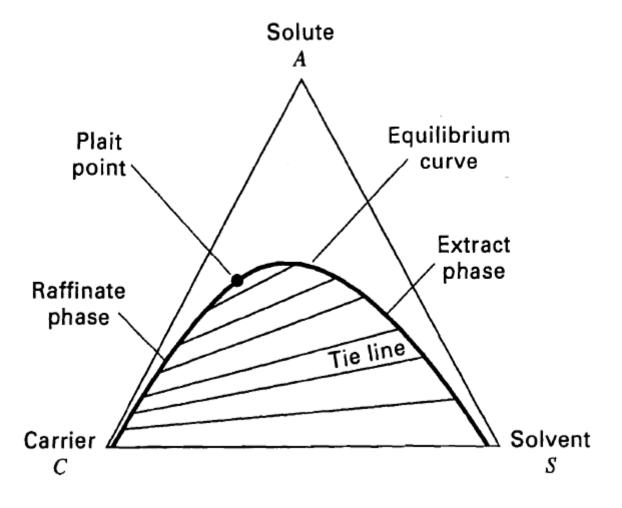
#### ■ In the above phase LL phase diagram:

- The pair of components of A and B are partially miscible.
- The pair of components A and C are completely miscible.
- The pair of components B and C are completely miscible.

**Example:** Water(A)-Chloroform(B)-Acetone(C)

#### Common classes of ternary liquid-liquid systems

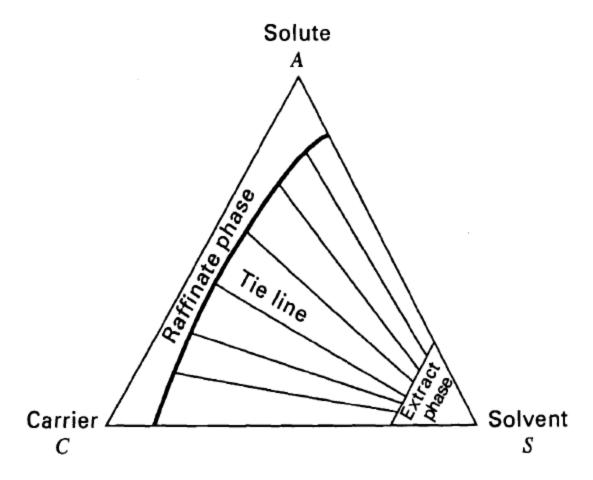
One immiscible or partially miscible pair:



C-S pair is partially miscible

## **Common classes of ternary liquid-liquid systems**

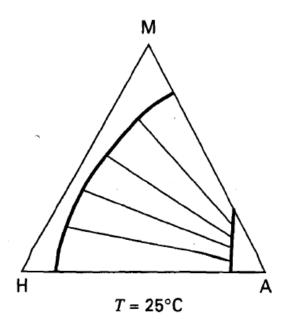
Two immiscible or partially miscible pairs

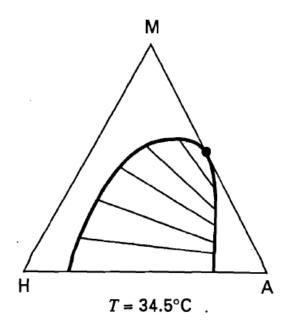


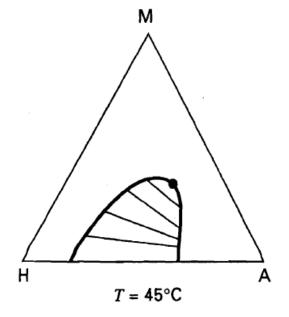
C-S and A-S pairs are partially miscible pair C-A is completely miscible

## Effect of temperature on liquid-liquid phase diagram

As shown in the figure below, phase diagram varies with temperature variation:







## Phase diagram and the range of feed composition that can be extracted

## **Example:**

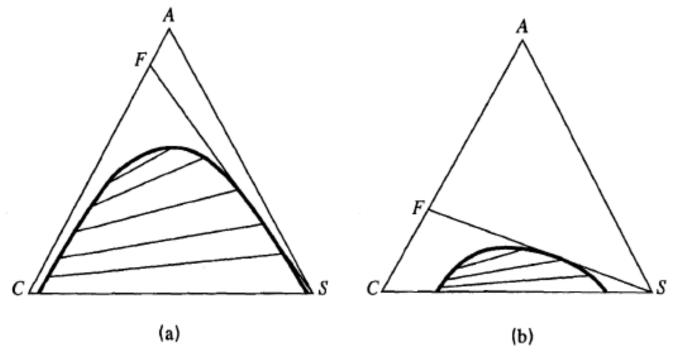


Figure 8.11 Effect of solubility on range of feed composition that can be extracted.

Phase diagram in (a) has a wider range of feed composition than that of (b)

## Phase diagram on rectangular coordinates

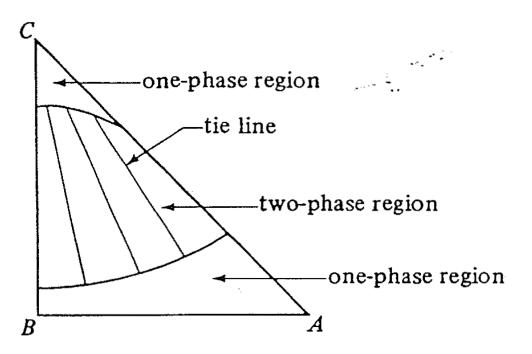


FIGURE 12.5-4. Phase diagram where the solvent pairs B-C and A-C are partially miscible.

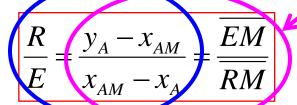
#### Lever-arm Rule

■Total mass balance:

$$R+E=M$$

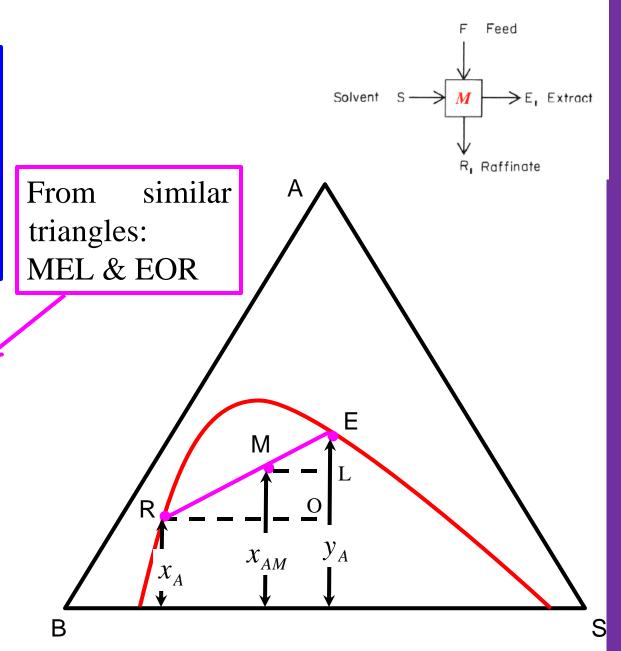
■Component A MB:

$$Rx_A + Ey_A = Mx_{AM}$$

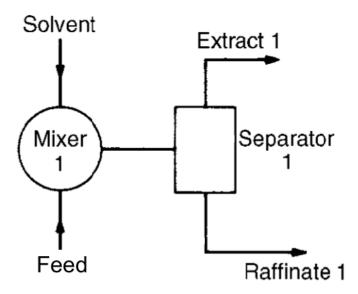


$$\frac{R}{M} = \frac{y_A - x_{AM}}{x_{AM} - x_A} = \frac{\overline{EM}}{\overline{RE}}$$

$$\frac{E}{M} = \frac{y_A - x_{AM}}{x_{AM} - x_A} = \frac{\overline{RM}}{\overline{RE}}$$



## One-stage extraction calculations Solvent

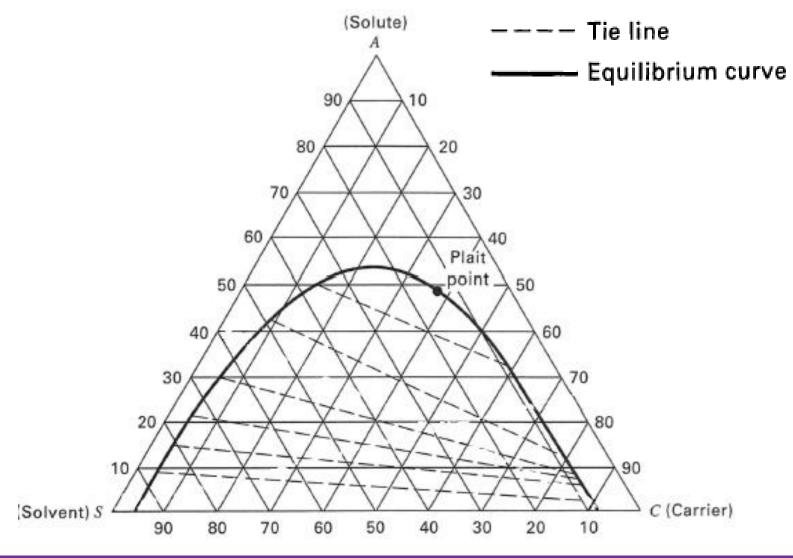


**Example.** In mixer-settler extraction unit, 250 kg of feed which contains 24 wt% solute(A) 76 wt% carrier(C) is mixed with pure 100 kg solvent (S).

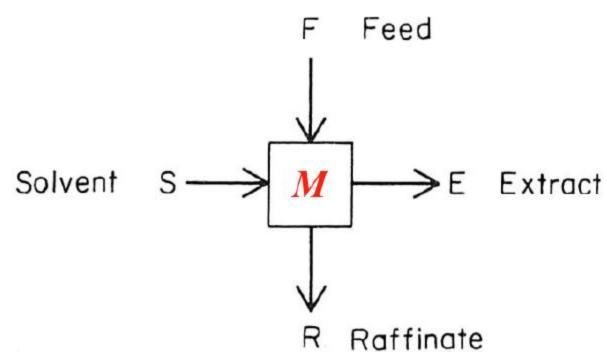
- 1) Find the overall composition of mixture at equilibrium using:
- a) The phase diagram given below
- b) Mass balances
- 2) Find the amounts and compositions of raffinate and extract phases.

The phase diagram is given on the next slide.

# One stage extraction calculations **Example.**



**Solution** 



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

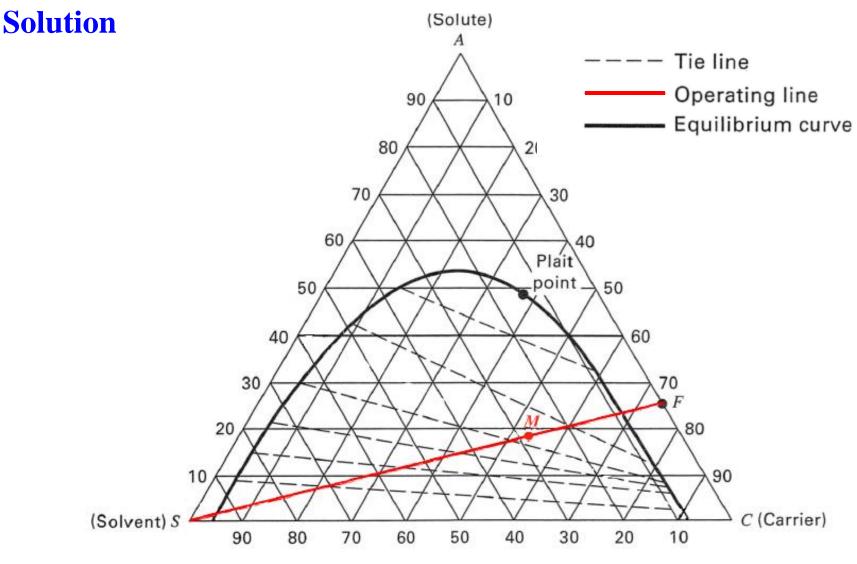
#### **Solution**

## Overall composition of mixture using phase diagram

- Locate the feed point (F) on the phase diagram
- Locate the solvent point (S) on the phase diagram
- Connect them by straight line (**operating line**).
- The mixing point must be on operating line, locate it:
  - Apply total mass balance: M = S + F = 100 + 250 = 350 kg
  - Measure the distance SF using the ruler
  - Apply lever-arm rule:

$$\frac{S}{M} = \frac{100}{350} = 0.2857 = \frac{\overline{MF}}{\overline{SF}}$$

- get  $\overline{MF}$  to locate M.
- Read the mixture composition



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

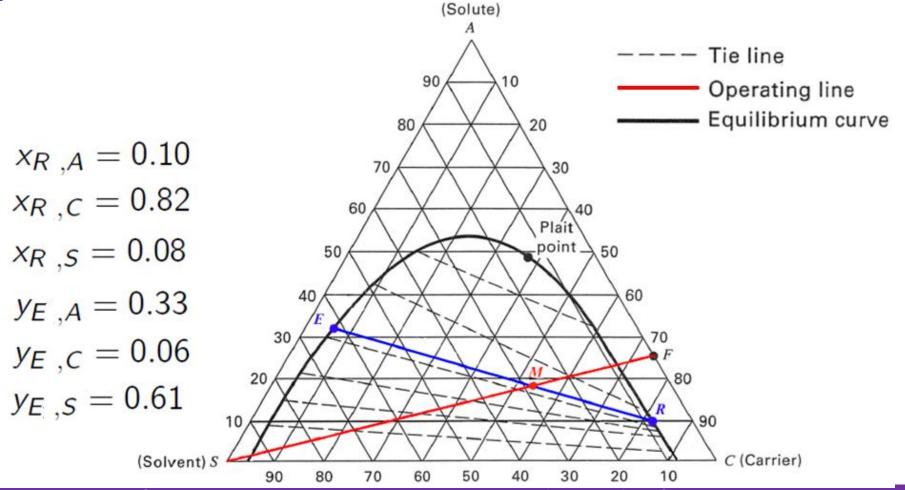
#### **Solution**

## Overall composition using mass balances:

Feed	Solvent	
F = 250  kg $S = 100  kg(x_A)_F = 0.24 (x_A)_S = 0.00(x_C)_F = 0.76 (x_C)_S = 0.00(x_S)_F = 0.00 (x_S)_S = 1.00$	M = F + S = 250 + 100 = 350  kg $(x_A)_M M = (x_A)_F F + (x_A)_S S$ = 0.24(250) + 0(100) = 60  kg $(x_A)_M = 60/350 = 0.171$	
		$(x_C)_M M = (x_C)_F F + (x_C)_S S$ = 0.76(250) + 0(100) = 190  kg $(x_C)_M = 190/350 = 0.543$ $(x_S)_M M = (x_S)_F F + (x_S)_S S$ = 0(250) + 1(100) = 100  kg $(x_S)_M = 100/350 = 0.286$

### **Composition of raffinate and extract phases:**

- Interpolate the tie line that passes through the mixture point M.
- The read the composition of R and E phases.



#### **Solution**

- To find the amount of raffinate (R) and extract (E):
  - Apply lever rule:

$$\frac{R}{M} = \frac{R}{350} = \frac{\overline{ME}}{\overline{RE}}$$

- Measure the distances  $\overline{RE}$  and  $\overline{ME}$  using the ruler.
- Calculate R
- Apply overall mass balance to calculate E:

$$M = S + F = 100 + 250 = 350 \text{kg} = E + R$$

Answer: E = 128 kg; R = 222 kg

## Solute recovery for one stage extraction

**Recovery**≡ fraction of solute recovered in the extract

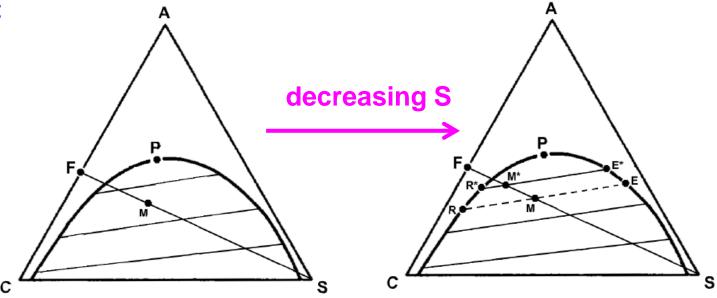
Solute recoverey= 
$$\frac{Fx_{F,A} - Rx_{R,A}}{Fx_{F,A}} = 1 - \frac{Rx_{R,A}}{Fx_{F,A}}$$

**Example.** Find the recovery in the previous example

Solute recoverey = 
$$1 - \frac{(222)(0.1)}{(250)(0.24)} = 63\%$$

## **Effect of solvent flow rate (S)**

#### **Illustration:**

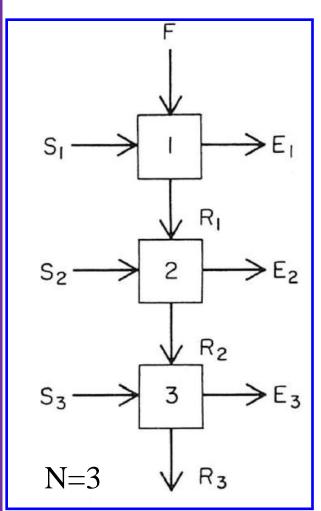


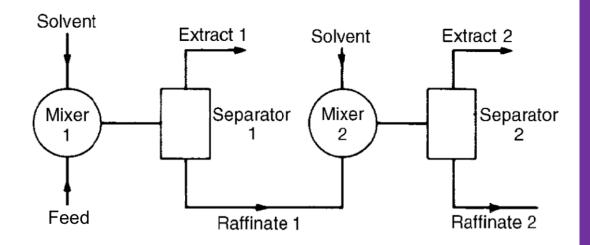
■ Based on the above phase diagram, as S decreases the mixture point M on the operating line will move toward the feed point F to be at new location M\*. This M\* has new equilibrium tie line at which:

$$X_{E^*,A} > X_{E,A}$$

(Solute concentration increases with S decrease)

 $x_{R*.A} > x_{R.A}$  (Solute recovery decreases with S decrease)





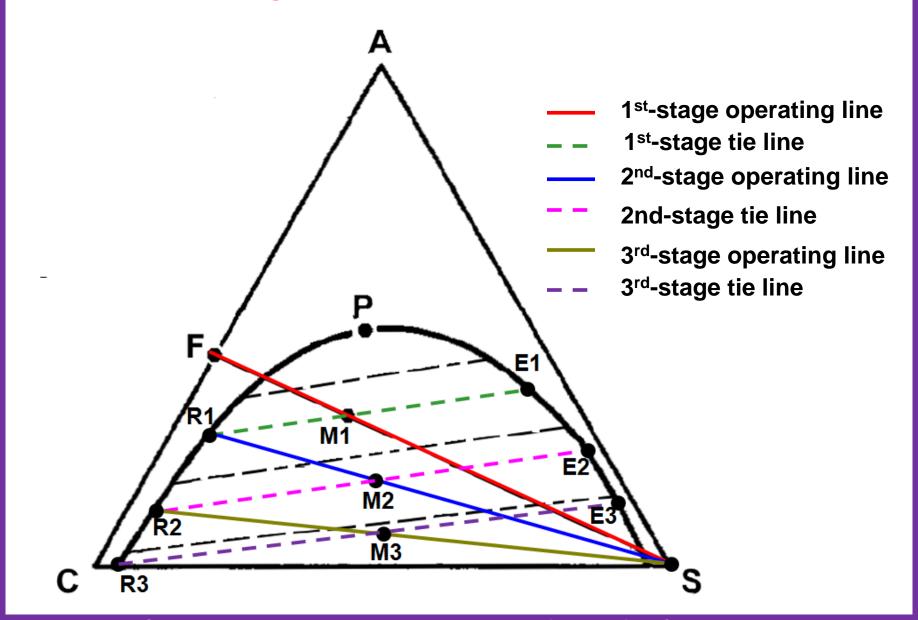
■ Recovery fraction of solute recovered

Solute recovery=
$$1 - \frac{R_N x_{R_N,A}}{F x_{F,A}}$$

N: number of stages

Overall solute concentration in the extract

$$\overline{y}_{E,A} = \sum_{i=1}^{N} E_i y_{E_i,A} / \sum_{i=1}^{N} E_i$$



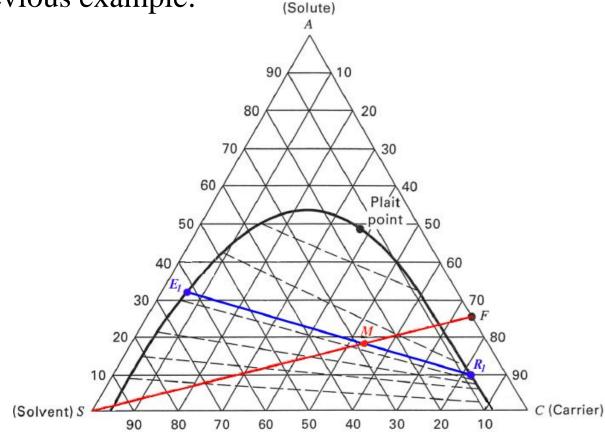
- Important questions arise:
  - What solvent flow rate?
  - How solvent flow rates are distributed among stages?
  - How many stages are required to...?

Trade off: solute recovery and overall solute concentration from the extract

**Example.** Cross-current mixer-settler extraction units are used for extraction process of 250 kg of feed which contains 24 wt% solute(A) and 76 wt% carrier(C). Each stage is supplied with pure 100 kg solvent (S). Find the minimum number of stages required to achieve at least 85% solute recovery. Find the corresponding overall solute concentration in the extract.

#### **Solution:**

First stage from previous example:



$$R_1 = 222 \text{kg};$$

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

$$x_{R_1,C} = 0.82;$$

$$x_{R_1,S} = 0.08$$

$$E_1 = 128 \text{kg}$$

$$y_{E_1,A} = 0.33$$

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

$$y_{E_1,S} = 0.61$$

#### **Solution:**

## **Second stage:**

 $\blacksquare$  Draw the operating line between  $R_1$ 

and S.

■ Measure  $R_1S$ 

■Use liver-arm rule:

$$\frac{R_1}{M_2} = \frac{R_1}{S + R_1}$$

$$= \frac{222}{322} = \frac{\overline{SM_1}}{\overline{R_1}S}$$

- Calculate:  $\overline{R_1S}$
- Locate M<sub>2</sub>

90 80 70 60 50 40 30 20 10 C (Carrier)

(Solute)

80

70

60

10

20

30

40

(Solvent) S

## Cross-current stage extraction Solution:

## **Second stage:**

- Interpolate the tie line for stage 2
- Read composition in R<sub>2</sub> and E<sub>2</sub>:  $x_{R_2,A} = 0.04$ ;  $x_{R_2,C} = 0.88$ ;  $x_{R_2,S} = 0.08$

$$y_{E_2,A} = 0.11; y_{E_2,C} = 0.05; y_{E_2,S} = 0.84$$

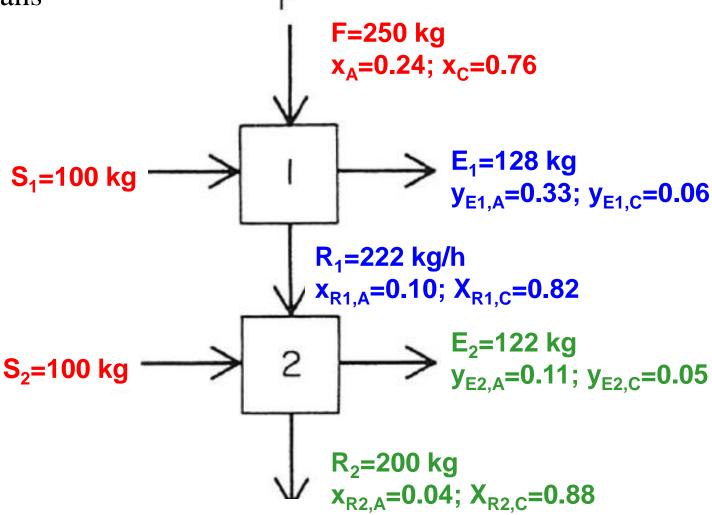
- Measure  $\overline{E_2R_2}$  and  $\overline{E_2M_2}$
- ■Apply lever arm rule to get R<sub>2</sub>:  $\frac{R_2}{M_2} = \frac{R_2}{S + R_1} = \frac{R_2}{322} = \frac{\overline{E_2 M_2}}{\overline{E_2 R_2}} \rightarrow R_2 = 200 \text{ kg}$  $E_2 = M_2 - R_2 = 122 \text{ kg}$
- Solute recoverey= $1 \frac{R_2 x_{R_2,A}}{F x_{F,A}} = 1 \frac{(200)(0.04)}{(250)(0.24)} = 87\% > 0.85 (required)$

Thus, two stages is sufficient to achieve the required solute recovery.

• Overall solute concentration:

$$\overline{y}_{E,A} = \sum_{i=1}^{2} E_i y_{E_i,A} / \sum_{i=1}^{N} E_i = (E_1 y_{E_1,A} + E_2 y_{E_2,A}) / (E_1 + E_2) = 0.22$$

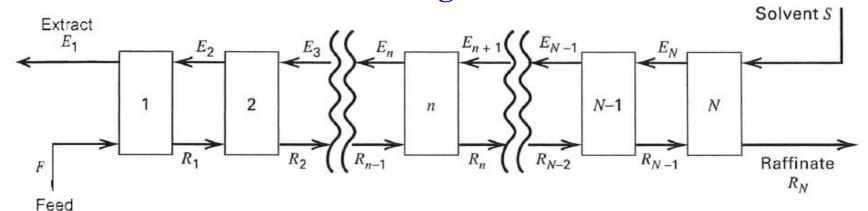
Use mass balances on the overall system and on each stage to verify the ans



**Exercise**. Consider a system for which you have been given the ternary diagram . A = solute, S = solvent (100% pure), C = carrier. For the overall two-stage cross-current system, the feed, F enters at 112 kg/hr with composition of 25 wt% solute and 75 wt% carrier. Each stage is provided with pure solvent of 50 kg/h. Find:

- a. Overall recovery [answer: 93%].
- b. Overall concentration of combined extract streams [answer: 21%]

### N units in counter-current arrangement:

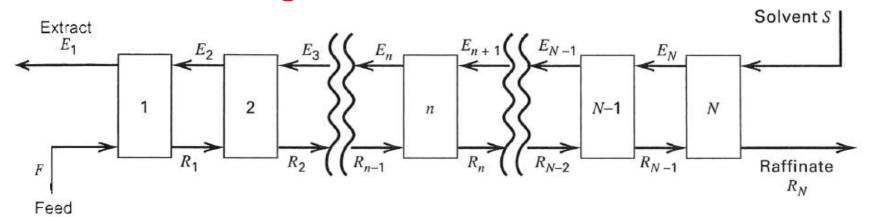


n: index for stage number

- "Re-use" of solvent
- $E_n$  and  $R_n$  for n=1,...N leaving each stage are in equilibrium [they are determined via the **tie line**]
- Solute Recovery:

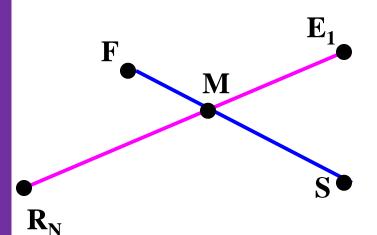
Solute recovery=
$$1 - \frac{R_N x_{R_N,A}}{F x_{F,A}}$$

■ Overall solute concentration:  $\overline{y}_{E,A} = y_{E_1,A}$ 

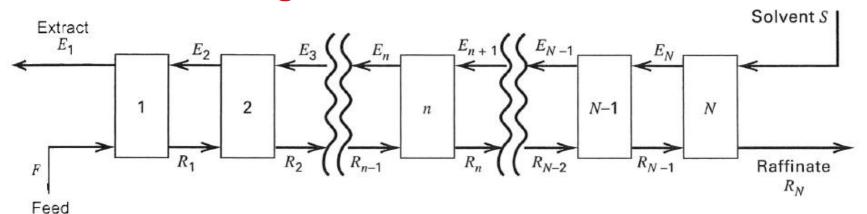


## Apply st. st. total mass balance on the overall system:

$$F + S = E_1 + R_N = M$$
  $\rightarrow$  Lever-arm rule:



- F, S, and M must located on the same straight line and mixture point M is between F and S.
- $E_1$ ,  $R_N$ , and M must located on the same straight line and mixture point M is between  $E_1$  and  $R_N$ .



## Apply total mass balance on each stage:

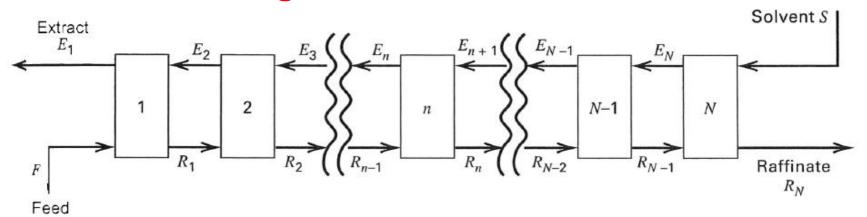
**First stage:** 
$$F + E_2 = E_1 + R_1 \text{ or } F - E_1 = R_1 - E_2$$

**Second stage:** 
$$E_2 + R_2 = E_3 + R_1$$
;  $or R_1 - E_2 = R_2 - E_3$ 

and in general for stages n = 2,...,N-1

$$E_n + R_n = E_{n+1} + R_{n-1}$$
;  $n = 2,..., N-1$  or  $R_{n-1} - E_n = R_n - E_{n+1}$ 

**Last stage:** 
$$R_{N-1} + S = E_N + R_N \text{ or } R_{N-1} - E_N = R_N - S$$

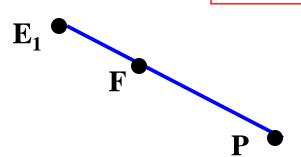


#### It is clear that

$$F - E_1 = R_1 - E_2 = R_2 - E_3 = \dots = R_{N-1} - E_N = R_N - S = Cons \tan t = P$$

This means that each flow difference is equal to P

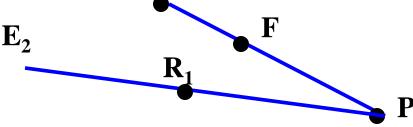
**Rearrange as :**  $F = E_1 + P$ 



 $\rightarrow$  Lever-arm rule, the three points F, E<sub>1</sub>, and P must located on the same straight line and F is between E<sub>1</sub> and P

P: operating point

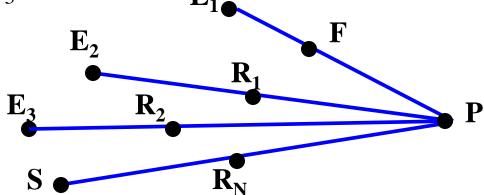
 $R_1 = E_2 + P$   $\rightarrow$  Lever-arm rule, the three points  $R_1$ ,  $E_2$ , and P must located on the same straight line and  $R_1$  is between  $E_2$  and P



 $R_2 = E_3 + P$   $\rightarrow$  Lever-arm rule, the three points  $R_2$ ,  $E_3$ , and P must located on the same straight line and  $R_2$  is between  $E_3$  and P

....and so on to:

$$R_N = S + P$$



## **General procedure:**

- 1. Connect S and F points with a line.
- 2. Locate the mixture point M using overall mass balance and lever rule.
- 3. Either specify  $E_1$  or  $R_N$  (we will always know one of them)
- 4. Connect a straight line through M and passing through the one specified  $(E_1 \text{ or } R_N)$ . Cross line with the equilibrium curve give the unspecified one.
- 5. Locate the operating point P:
  - Connect S through R<sub>N</sub> and extrapolate
  - Connect E<sub>1</sub> through F and extrapolate
  - Cross lines at operating point P
- 6. In general: connect  $E_n$  and  $R_n$  via equilibrium tie lines

**Example.** Consider a system for which you have been given the ternary diagram . A = solute, S = solvent (100% pure), C = carrier. In a counter-current extraction process, the feed, F enters at 112 kg/hr with composition of 25 wt% solute and 75 wt% carrier. The solvent flow rate is 28 kg/hr.

- a. Find the number of theoretical stages required to achieve solute concentration in raffinate of 2.5 wt% (at most).
- b. Calculate the overall recovery and solute concentration of the extract stream.
- c. Plot solute concentrations in the extract and raffinate streams versus stages number.

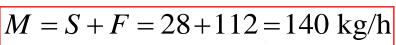
$$S = 28 \text{ kg/h}$$
;  $F = 112 \text{ kg/h}$ ;  $x_{R_N,A} = 0.025$ ;  $x_{F,A} = 0.25$ ;  $x_{F,C} = 0.75$ 

10

(Solvent) S

**Step 1 and 2:** Connect S and F points with a line and locate M.

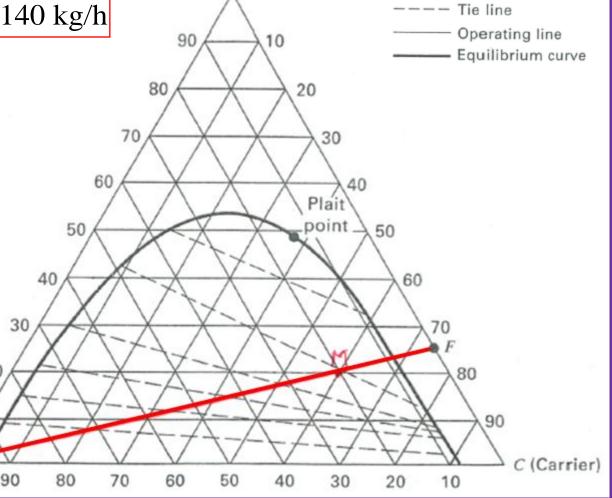
(Solute)



- Measure  $\overline{SF}$
- Lever rule:

$$\frac{S}{M} = \frac{\overline{MF}}{\overline{SF}}$$

■ Determine:*MF* 



## **Step 3 and 4:** specify E<sub>1</sub>

■ Locate the point  $R_N$  ( $x_{R_N,A} = 0.025$ )

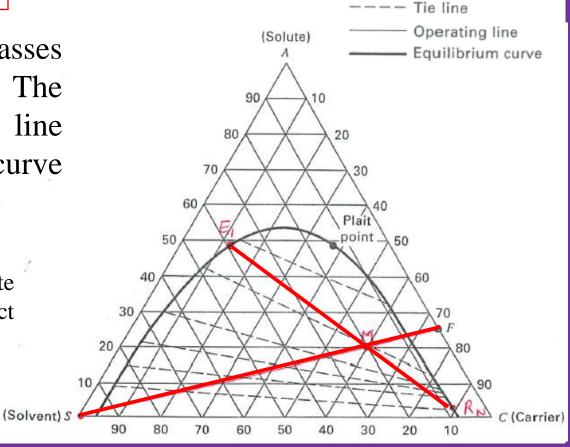
$$M = E_1 + R_N = 140 \text{ kg/h}$$

• Draw the line passes through M and  $R_N$ . The position at which the line crosses the equilibrium curve is  $E_1$ 

**Read**  $y_{E_1,A} = 48\%$ 

This is the overall solute concentration of the extract stream:

$$\bar{y}_{E,A} = y_{E_1,A} = 48\%$$



## Step 3 and 4: specify E<sub>1</sub>

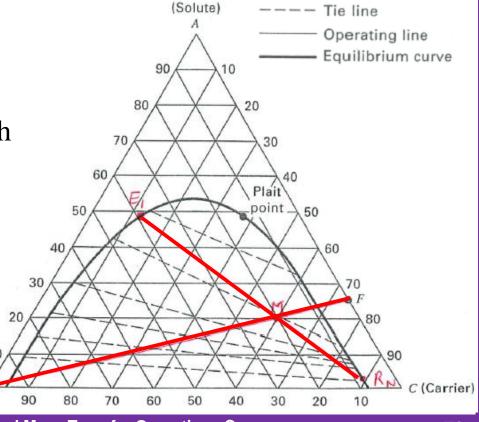
- Measure  $\overline{E_1R_N}$  and  $\overline{ME_1}$
- Lever rule:

$$\frac{R_N}{M} = \frac{R_N}{140} = \frac{ME_1}{E_1 R_N} = 0.62$$

$$\to R_N = 87 \text{ kg/h}$$

$$E_1 = M - R_N = 140 - 87 = 53 \text{ kg/h}$$

Recovery=
$$1 - \frac{R_N x_{R_N,A}}{F x_{F,A}}$$
  
=  $1 - \frac{(87)(0.025)}{(112)(0.25)} = 0.92\%$ 



(Solvent) S

## Step 3 and 4: specify E<sub>1</sub>

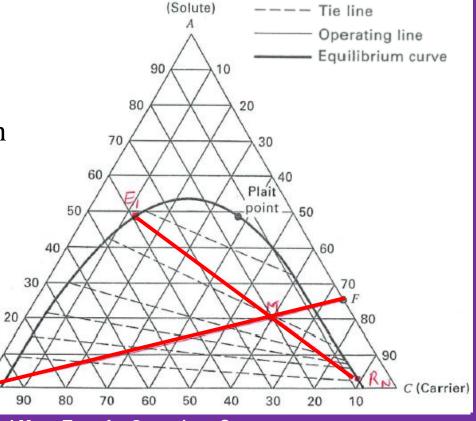
- Measure  $\overline{E_1R_N}$  and  $\overline{ME_1}$
- Lever rule:

$$\frac{R_N}{M} = \frac{R_N}{140} = \frac{ME_1}{E_1 R_N} = 0.62$$

$$\to R_N = 87 \text{ kg/h}$$

$$E_1 = M - R_N = 140 - 87 = 53 \text{ kg/h}$$

Recovery=
$$1 - \frac{R_N x_{R_N,A}}{F x_{F,A}}$$
  
=  $1 - \frac{(87)(0.025)}{(112)(0.25)} = 0.92\%$ 



(Solvent) S

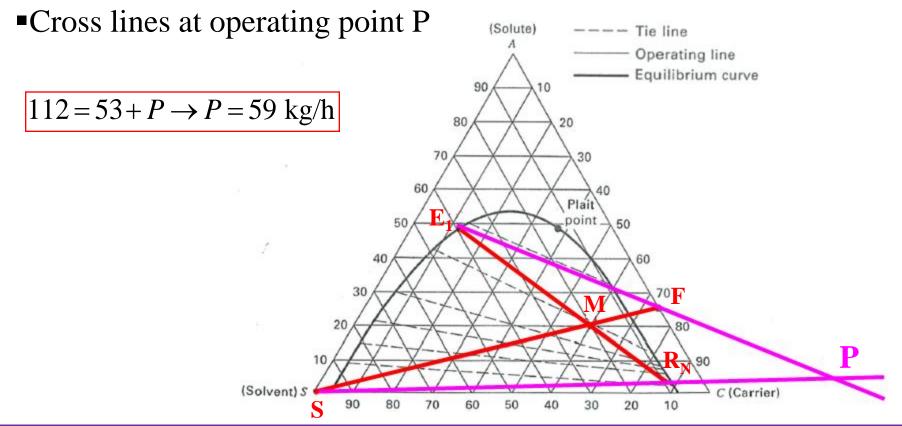
**Step 5**: specify the operating point P

$$F = E_1 + P$$

 $F = E_1 + P$  • Connect  $E_1$  through F and extrapolate

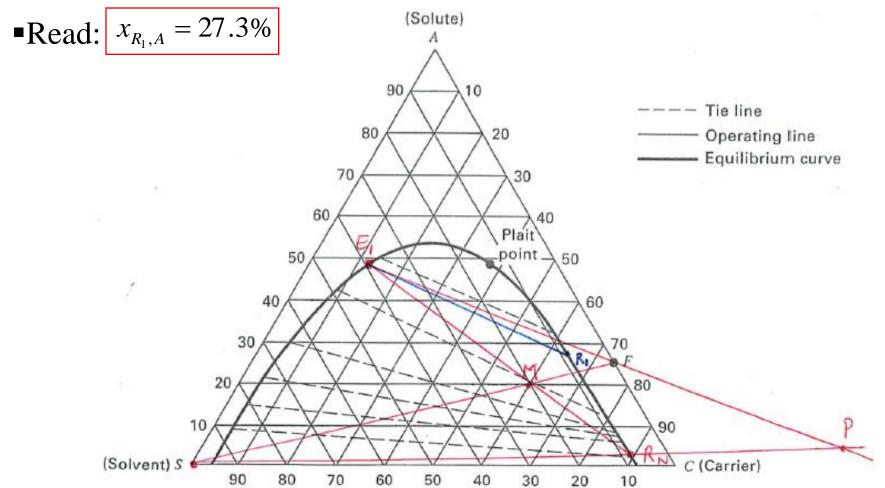
$$R_N = S + P$$

 $R_N = S + P$  • Connect S through  $R_N$  and extrapolate



**Step 6:** In general: connect  $E_n$  and  $R_n$  via equilibrium tie lines

■ Connect  $E_1$  with  $R_1$  via equilibrium tie lines

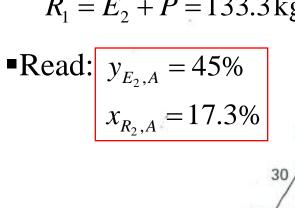


- Connect  $R_1$  with P to extrapolate  $E_2$
- Connect E<sub>2</sub> with R<sub>2</sub> via tie line
- Lever rule:

$$\frac{E_2}{P} = \frac{E_2}{59} = \frac{\overline{R_1 P}}{\overline{E_2 R_1}} = 1.26$$

 $\rightarrow E_2 = 74.3 \text{ kg/h}$ 

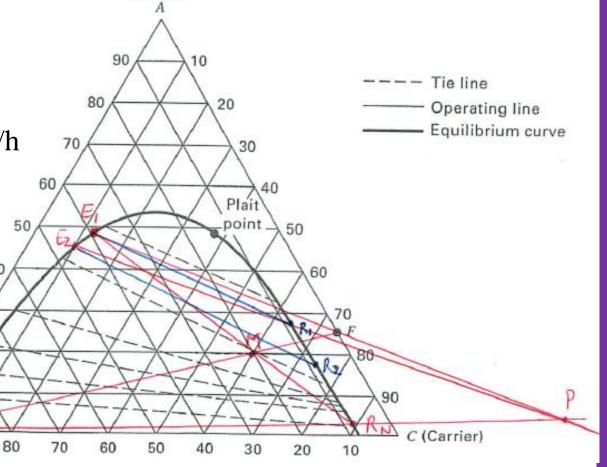
 $R_1 = E_2 + P = 133.3 \text{ kg/h}$ 



(Solvent) S

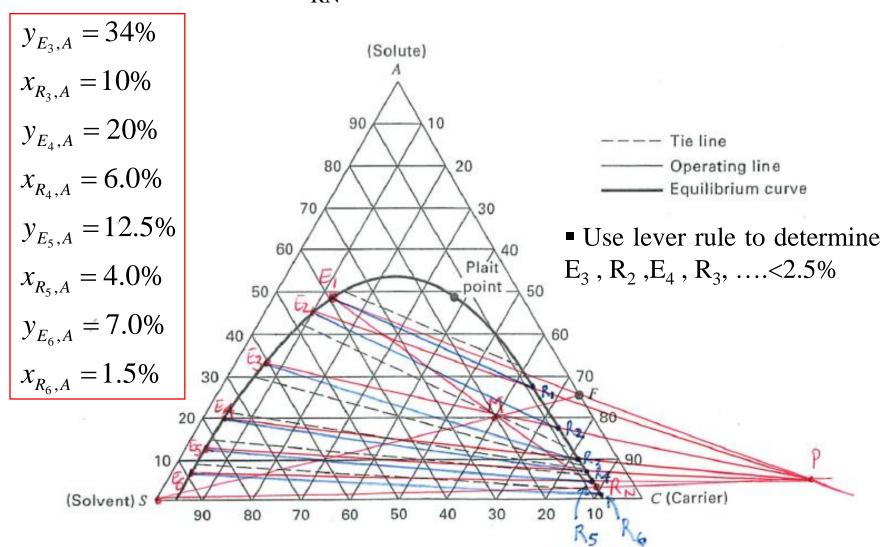
10

90



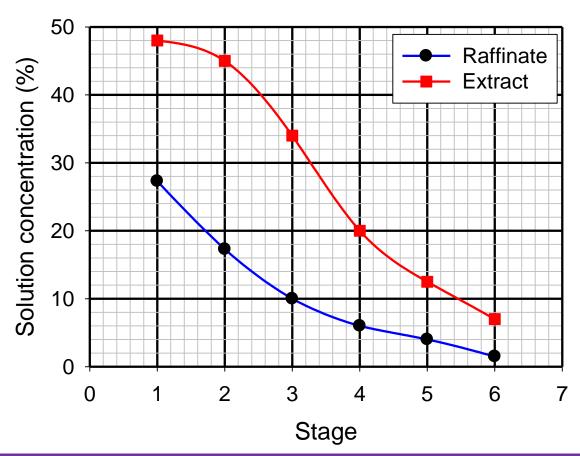
(Solute)

■ Continue to reach  $x_{RN} \le 2.5\%$ 



$$x_{R_6,A} = 1.5\% < 2.5\%$$

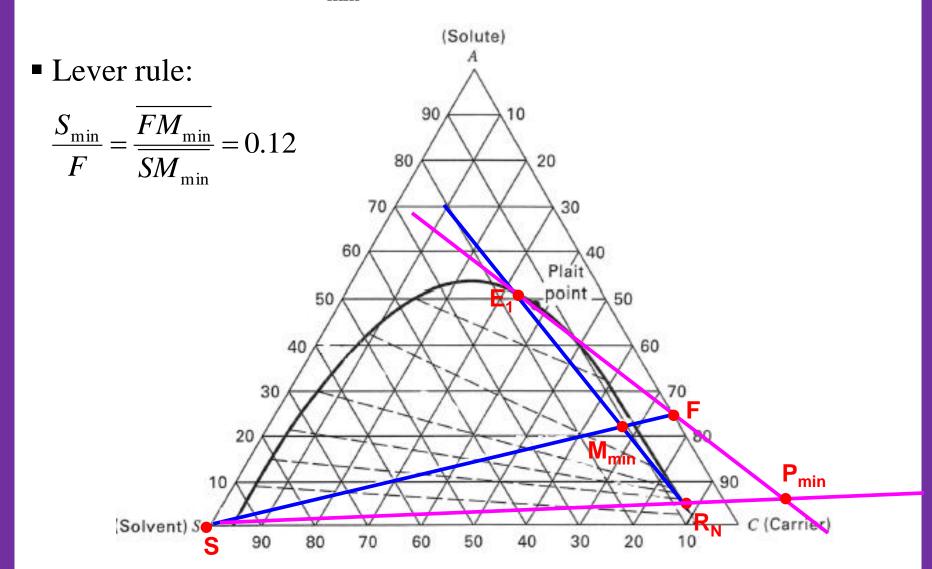
N=6 theoretical stages is enough to have solute concentration less than 2.5 wt% in raffinate stream



- **Determination of minimum solvent-to-feed ratio**  $(S_{min}/F)$ :
  - $\rightarrow$  If  $x_{RN,A}$  is given:
  - Connect F and S with straight line on ternary phase diagram.
  - Connect S and  $R_N$  with straight line on ternary phase diagram.
  - Search for  $E_1$  point on equilibrium curve such that:
    - $E_1R_N$  line intersects with SF line at mixing point with the minimum possible distance about F (maximum possible distance from S. This mixing point is denoted as  $M_{min}$ .
    - $E_1F$  line must intersects with  $SR_N$  at the operating point denoted as  $P_{\min}$ .
  - $\rightarrow$  If  $E_1$  is given, similar search approach for  $R_N$  can be followed.

**Remark.** With  $S_{min}/F$ , the required number of theoretical stages:  $N{\rightarrow}\infty$ 

**Example.** Determine  $S_{min}/F$  for the system of previous example

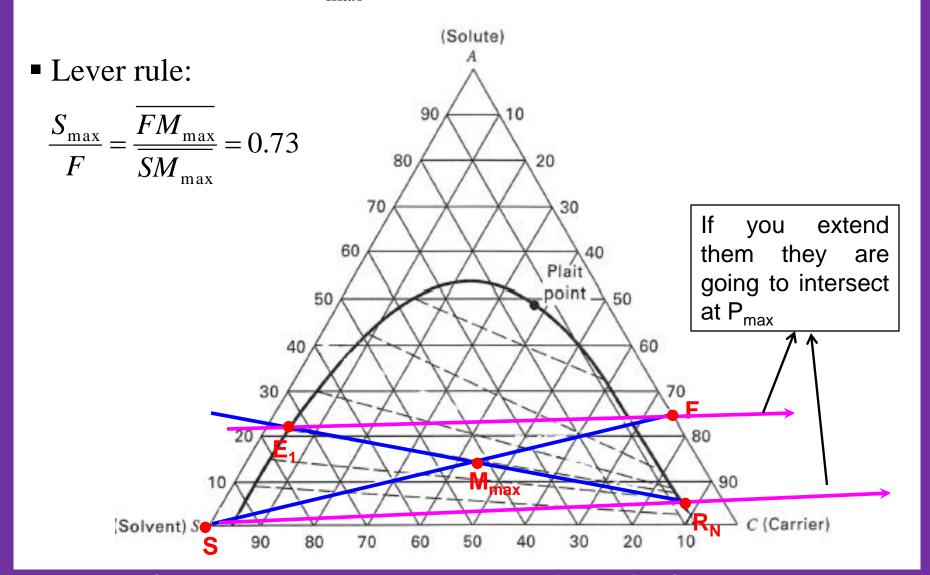


- **Determination of maximum solvent-to-feed ratio**  $(S_{max}/F)$ :
  - $\rightarrow$  If  $x_{RN,A}$  is given:
  - Connect F and S with straight line on ternary phase diagram.
  - Connect S and  $R_N$  with straight line on ternary phase diagram.
  - Search for  $E_1$  point on equilibrium curve such that:
    - $E_1R_N$  line intersects with SF line at mixing point with the maximum possible distance from F (minimum possible distance from S. This mixing point is denoted as  $M_{max}$ .
    - $E_1F$  line must intersects with  $SR_N$  at the operating point denoted as  $P_{\rm max}$ .
  - $\rightarrow$  If  $E_1$  is given, similar search approach to locate  $R_N$  can be followed.

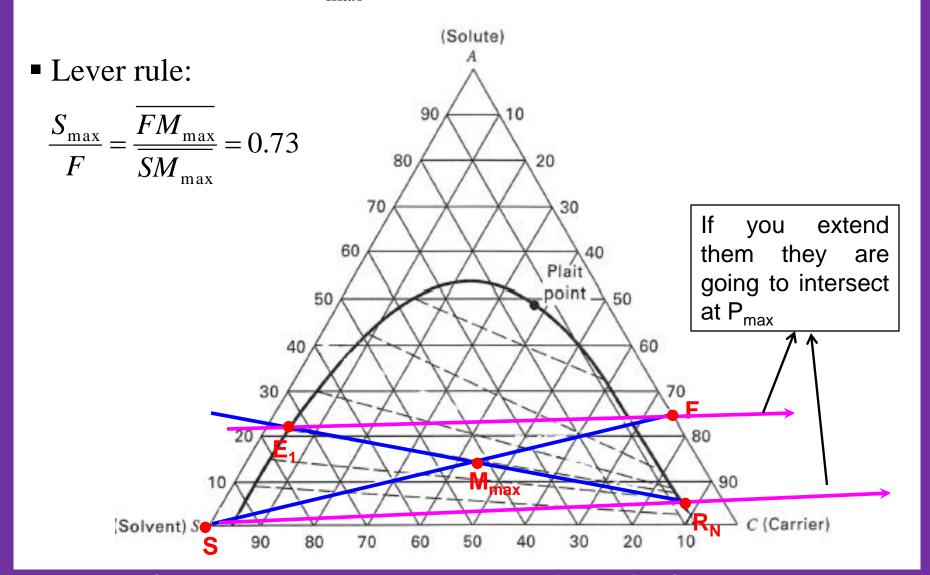
**Remark.** With  $S_{max}/F$ , the required number of theoretical stages:

 $N\rightarrow 1$ 

**Example.** Determine  $S_{max}/F$  for the system of previous example



**Example.** Determine  $S_{max}/F$  for the system of previous example



#### Remark.

- For extraction operation:  $\left(\frac{S_{\min}}{F}\right) < \left(\frac{S}{F}\right) < \left(\frac{S_{\max}}{F}\right)$  or  $S_{\min} < S < S_{\max}$
- A reasonable value :  $S \approx 1.5 S_{\min}$

**Example.** For previous example, check if the flow rate of solvent (S=28 kg/h) is reasonable for the given feed flow rate (F=112 kg/h).

$$S_{\min}/F = 0.12 \rightarrow S_{\min} = 0.12F = (0.12)(112) = 13.4 \text{ kg/h}$$

A reasonable value: 
$$S \approx 1.5 S_{min} = 20.1 \text{kg/h}$$

Thus, the solvent flow rate of (S=28 kg/h) is a little bit higher than the reasonable one.

**Exercise.** Resolve the previous exampleS= 20 kg/h to calculate the required number of theoretical stages.

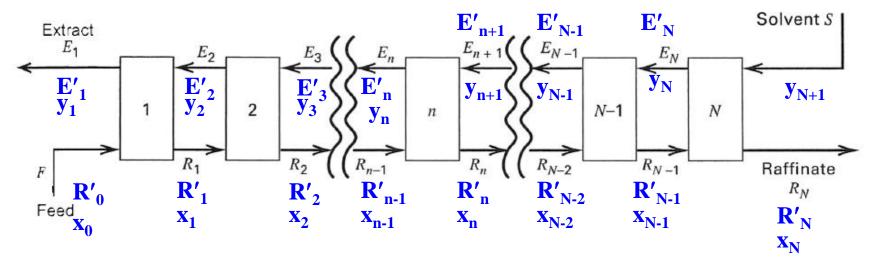
- The carries (B) of solute (A) is immiscible in solvent (S).
- In other words, solute is the only component distributed in extract and raffinate.
- This means that the raffinate has a binary mixture of A and B and the extract has binary mixture of A and S.
- In such ternary coordinates is not helpful.
- As in distillation and absorption, the equilibrium xy diagram is used instead.
- Let

x :solute concentration in raffinate

y: solute concentration in extract

E': flow rate of solvent in the extract streams

R': flow rate of carrier B in the raffinate streams



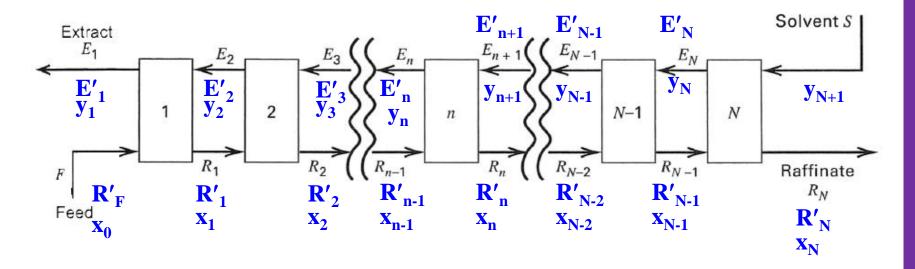
Applying mass balance for carries B on each stage gives:

$$R'_0 = (1 - x_0)F = R'_1 = R'_2 = \dots = R'_2 = \text{constant} = R'$$

Applying mass balance for solvent S on each stage gives:

$$E'_1 = E'_1 = E'_2 = \dots = E'_N = (1 - y_{N+1})S = \text{constant} = E'$$

If pure solvent is used:  $y_{N+1} = 0 \Rightarrow E' = S$ 



■ Applying mass balance for solute A over stages:  $1\rightarrow n$ :

$$R'\left(\frac{x_0}{1-x_0}\right) + E'\left(\frac{y_{n+1}}{1-y_{n+1}}\right) = R'\left(\frac{x_n}{1-x_n}\right) + E'\left(\frac{y_1}{1-y_1}\right)$$

- Let us now define:
  - The solute-to-carrier mass ratio in the raffinate:

$$X = \frac{x}{1 - x} = \frac{\log \text{ solute A}}{\log \text{ carrier B}}$$

•and solute-to-solvent mass ratio in the extract:

$$Y = \frac{y}{1 - y} \left[ = \right] \frac{\text{kg solute A}}{\text{kg solventS}}$$

■ Using such mass ratio, the overall mass balance for solute A over stages: 1→n becomes:

$$E'Y_{n+1} = R'X_n + E'Y_1 - R'X_0$$

■ **Dividing by E' gives:**  $Y_{n+1} = \frac{R'}{E'} X_n + Y_1 - \frac{R'}{E'} X_0$ 

### **Operating line equation**

$$Y_{n+1} = \frac{R'}{E'} X_n + Y_1 - \frac{R'}{E'} X_0$$

- For the above operating line equation:
  - Plot of  $Y_{n+1}$  versus  $X_n$  on X-Y diagram gives a straight line with:

Slope = 
$$\frac{R'}{E'}$$
 Intercept=  $Y_1 - \frac{R'}{E'} X_0$ 

• For certain feed flow rate, the minimum solvent flow rate,  $S_{min}$  must correspond to the maximum allowable slope:

$$E'_{\min} = \frac{R'}{\text{Slope}_{\max}}$$

But 
$$(1 - y_{N+1})S = E' \Rightarrow S_{\min} = \frac{E'_{\min}}{(1 - y_{N+1})} = \frac{R'}{(1 - y_{N+1})(Slope_{\max})}$$

• If x and y are quite small(dilute solutions):  $X \approx x$ ;  $Y \approx y$ 

**Example.** An inlet water solution of 100 kg/h containing 0.01 wt fraction nicotine (A) in water is stripped with kerosene stream of 200 kg/h containing 0.0005 wt fraction nicotine in a countercurrent stage tower. The water and kerosene are essentially immiscible in each other. It is desired to reduce the concentration of exit water to 0.0010 wt fraction nicotine. Determine.

- a. Number of the theoretical stages needed.
- b. The minimum solvent rate.

The equilibrium data are as follows:

X	I/
	0.00000
0.001010	0.000806
0.002460	0.001959
0.005000	0.004540
0.007460	0.006820
0.009880	0.009040
0.020200	0.018500

#### Solution.

■ Solute (A)  $\equiv$  Nicotine; Carrier (B)  $\equiv$  Water Solvent (S)  $\equiv$  Kerosene

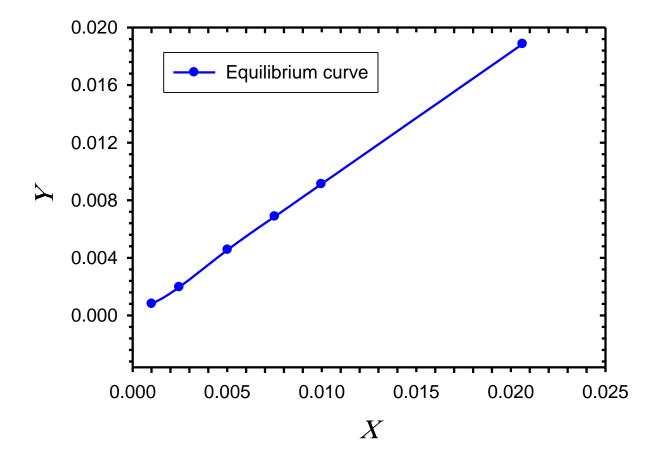
$$F = 100 \text{ kg/h}$$
;  $S = 200 \text{ kg/h}$   
 $x_0 = 0.01$ ;  $x_N = 0.001$ ;  $y_{N+1} = 0.0005$ 

■Re-describe the equilibrium data in terms of solute-to-carrier mass ratio (X) and solute-to-solvent mass ratio in the raffinate

X=x/(1-x)	Y = y/(1-y)
0.001011	0.000807
0.002466	0.001963
0.005025	0.004561
0.007516	0.006867
0.009979	0.009122
0.020616	0.018849

■ Draw *XY* equilibrium curve

Solution.



Solution.

$$F = 100 \text{ kg/h}$$
;  $S = 200 \text{ kg/h}$   
 $x_0 = 0.01$ ;  $x_N = 0.001$ ;  $y_{N+1} = 0.0005$ 

### Draw the operating line:

- 1. Calculate flow rate of water:  $R' = (1 x_0)F = 99.0 \text{ kg/h}$
- 2. Calculate flow rate of solvent (Kerosene):

$$E' = (1 - y_{N+1})S = 200 (1 - 0.0005) = 199.9 \text{ kg/h}$$

3. Find the slope of operating line equation:

Slope = 
$$R'/E' = 0.50$$

4. Calculate: 
$$X_0 = x_0 / (1 - x_0) = 0.01$$
  
 $X_N = x_N / (1 - x_N) = 0.001$   
 $Y_{N+1} = y_{N+1} / (1 - y_{N+1}) = 0.0005$ 

#### Solution.

5. Determine  $Y_1$ . The point  $(X_N, Y_{N+1}) = (0.001, 0.0005)$  must lies on the operating line, thus

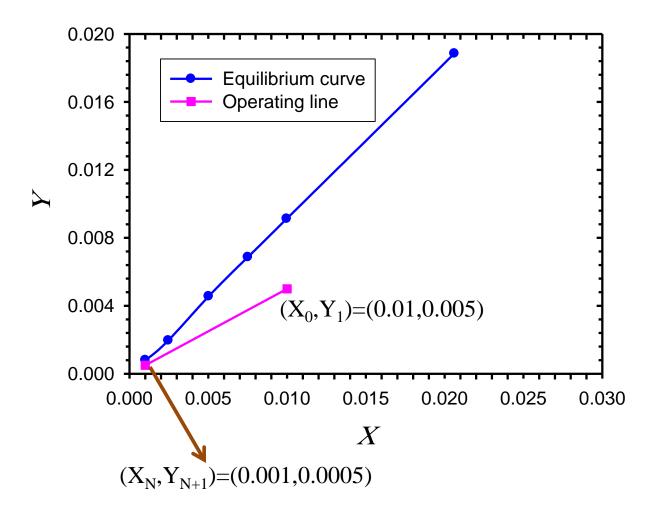
$$Y_{N+1} = \frac{R'}{E'} X_N + Y_1 - \frac{R'}{E'} X_0$$

$$0.0005 = (0.50)(0.001) + Y_1 - (0.50)(0.01) \rightarrow Y_1 = 0.005$$

The point  $(X_0,Y_1)=(0.01,0.005)$  must also must lies on the operating line.

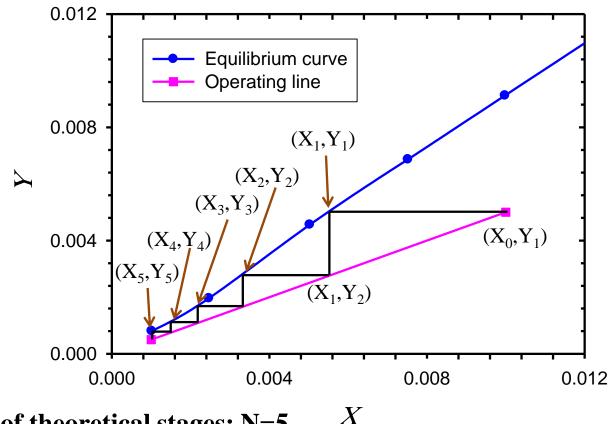
6. With the two point:  $(X_N, Y_{N+1}) = (0.001, 0.0005)$  and  $(X_0, Y_1) = (0.01, 0.005)$  we can now draw the operating line.

Solution.



#### Solution.

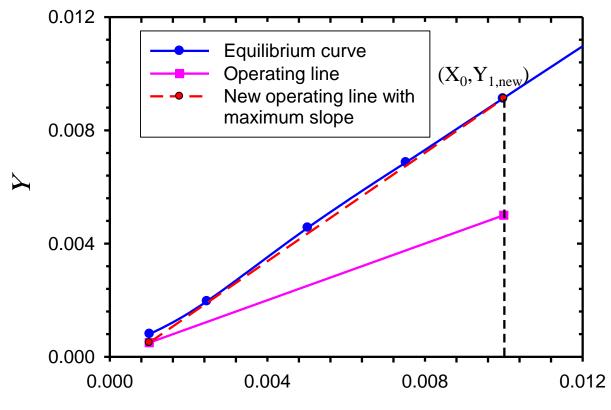
■ The number of theoretical stages are stepped off, as in distillation and absorption, from as  $(X_0, Y_1)$  to  $(X_N, Y_{N+1})$ :



a) The number of theoretical stages; N=5

#### Solution.

b) Minimum solvent flow → Maximum allowable slope



Slope<sub>max</sub> = 
$$\frac{Y_{1,\text{new}} - Y_{N+1}}{X_0 - X_N} = \frac{0.009122 - 0.0005}{0.01 - 0.001} = 0.96$$

#### Solution.

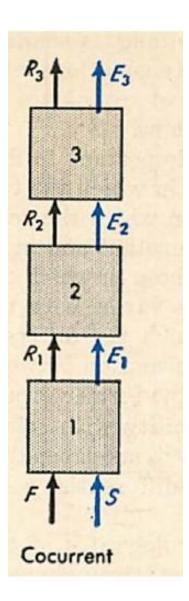
b) Minimum solvent flow → Maximum allowable slope

Slope<sub>max</sub> = 0.96 = 
$$\frac{R'}{E'_{min}}$$
 =  $\frac{99.0}{E'_{min}}$   $\rightarrow E'_{min}$  = 103.1 kg/h

$$E'_{\min} = 103.1 = S_{\min}(1 - y_{N-1}) = S_{\min}(1 - 0.0005)$$
  
 $\rightarrow S_{\min} = 103.1 \text{ kg/h}$ 

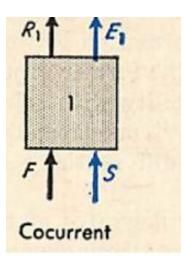
■ If reasonable solvent flow rate; S=1.5S<sub>min</sub>, for such process we should use around 155 kg/h. Try to find number of stages with this solvent flow rate.

### Cocurrent one stage extraction



$$M = S + F = R_1 + E_1 = R_2 + E_2 = \dots = R_N + E_N$$

Obviously, always there will be only one theoretical stage operating in cocurrent mode.



# Converting theoretical stages to actual equipment size

Assume the counter-current stage extraction needs 6 theoretical stages to achieve some required recovery:

- This does not mean we require 6 mixer-settlers (though we could do that, but costly).
- It means we need an extraction 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.
- Vendors: provide **HETS** = Height Equivalent to a Theoretical Stage.
- Use that to size the extraction column:  $H = -\frac{1}{2}$

$$H = \frac{\text{HETS} \times \text{N}}{\text{Stage efficiency}}$$

Where H is the height of extraction tower

# Converting theoretical stages to actual equipment size

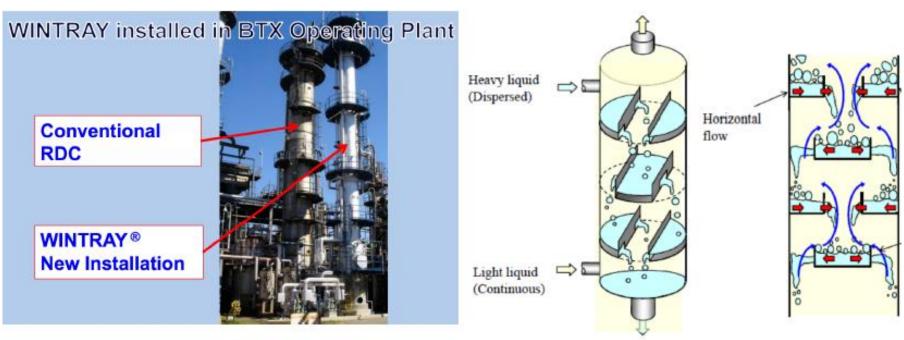


Figure 2: Concept and Flow of WINTRAY System

[WINTRAY (Japanese company; newly patented design)]

# Converting theoretical stages to actual equipment size

Туре	Capacity of	Approximate Flooding, $(V_D + V_C)$ , $m^3/m^2 \cdot h$	Spacing between Stages, T, cm	Overall Height of Transfer Unit, H <sub>OL</sub> , m	Plate Efficiency, E <sub>O</sub> , %	Height of Equilibrium Stage, HETS, m	Rej
Spray Tower	15-75			3-6		3-6	M4 S5
Packed Tower	12-30			0.9-1.7		0.4-1.5	\$4, \$5, W1
Structured Packing Tower	65-90					0.5-1.6	H4
Sieve- Tray Tower	27-60		10=25		8-30	0.8-1.2	M4, P4, S4
Pulsed Packed Tower	17–23	40				0.15-0.3	P4, S4, W1
Pulsed Sieve- Tray Tower	25-35	60	5.1			0.15-0.3	\$4. W1
Scheibel Tower	10-14*	40	2.5-20			0.1-0.3	P4, S2, S3, W1
Karr Tower	30-40	80-100	5-15			0.2-0.6	S2, S4