

# **Heat and Mass Transfer Operations**

# Lec 1: liquid-liquid Extraction-Part 1

#### Content

Introduction, Liquid-Liquid Extraction, Distribution Coefficients, Liquid-Liquid Equilibrium, Operating Modes of Extraction and calculations

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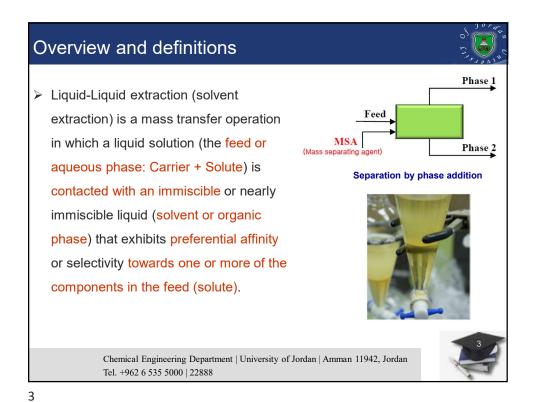
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#### Content

- Introduction
- Liquid-Liquid Extraction
- Distribution Coefficients
- Liquid-Liquid Equilibrium
- Operating Modes of Extraction and calculations



**Principal references:** Chapter 27 in C.J. Geankoplis book and Chapter 8 in Henley, Seader & Roper book



Overview and definitions



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



#### Overview and definitions



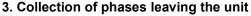
#### Three major steps required in LLE:

#### 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



split the raffinate from the extract



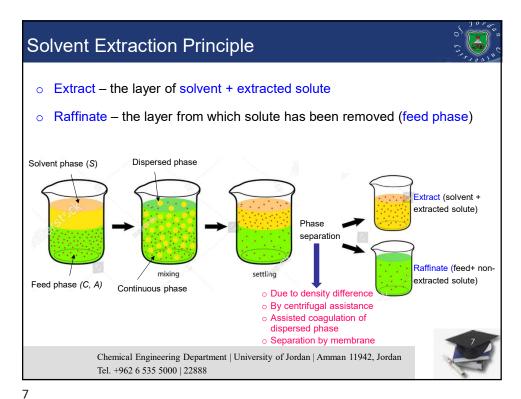
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### Solvent Extraction Principle



- The simplest liquid-liquid extraction involves only a ternary system.
  - The feed consists of two miscible components, the carrier (C) and the solute (A).
- Addition of a second phase (solvent phase, S)
- Components (C,S) are immiscible (do not dissolve in one another) or at most only partially soluble in each other.
- Immiscible liquids form two distinct phases when mixed.
- Solute (A) is soluble in (C) and completely or partially soluble in S.
- During the extraction process, mass transfer of (A) from the feed to the solvent occurs, i.e. solute molecules are distributed between phases, with less transfer of (C) to the solvent, or (S) to the feed.
- After extraction; the feed and solvent phases are called the Raffinate (R) and Extract (E) phases respectively.



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### Liquid-Liquid Extraction



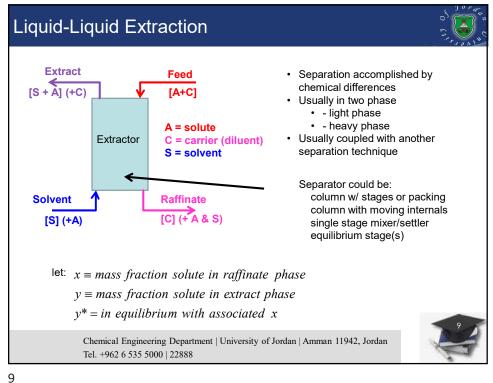
- Normally one of the two phases is an organic phase while the other is an aqueous phase.
- ➤ Under equilibrium conditions the distribution of solute *A* over the two phases is determined by the distribution law.

$$K_D = \frac{(y_A)_E}{(x_A)_R}$$



- > After the extraction the two phases can be separated because of their immiscibility.
- Component A is then separated from the extract phase by a technique such as distillation and the solvent is regenerated.
- ➤ Further extractions may be carried out to remove more component *A* .





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# Why Solvent Extraction?



Liquid-liquid extraction is used to separate components in situations where:

- 1. Relative volatilities are quite close to unity ( $\alpha$  < 1.1), or azeotropic making distillation very costly. (Distillation requires tall towers due to the existence of many trays, and high energy consumption because of high reflux ratios)
  - e.g. A mixture of benzene and cyclohexane. The normal boiling points of these organics are 80.1°C and 80.7°C, respectively, making their separation by distillation impractical
- 2. Thermally sensitive components will not permit high enough temperatures to produce a vapor-liquid system at reasonable pressures (pressures greater than 10-50 mm Hg).
- 3. When Solute concentration is low



### **Applications**

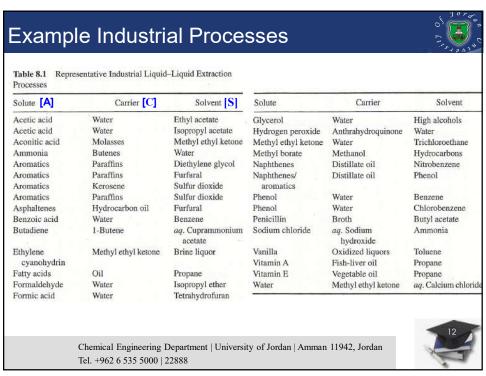


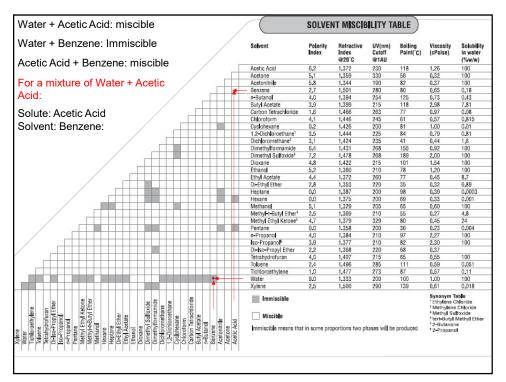
- Usual purpose, to remove products and pollutants from dilute aqueous streams (purify the Raffinate, or Solute)
- > Wash polar compounds or acids/bases from organic streams
- Example:
  - recovery of penicillin from fermentation broth solvent: butyl acetate
  - recovery of acetic acid (b.p 118°c) from dilute aqueous (b.p 100°c) solutions

solvent: ethyl-acetate

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Chemical	•Washing of acids/bases, polar compounds from organics			
Pharmaceuticals	Recovery of active materials from fermentation broths     Purification of vitamin products			
Effluent Treatment	Recovery of phenol, DMF, DMAC     Recovery of acetic acid from dilute solutions			
Polymer Processing	Recovery of caprolactam for nylon manufacture     Separation of catalyst from reaction products			
Petroleum	Lube oil quality improvement     Separation of aromatics/aliphatics (BTX)			
Petrochemicals	Separation of olefins/parafins     Separation of structural isomers			
Food Industry	Decaffeination of coffee and tea     Separation of essential oils (flavors and fragrances)			
Metals Industry	Copper production     Recovery of rare earth elements			
Inorganic Chemicals	• Purification of phosphoric acid			
Nuclear Industry	• Purification of uranium			

#### Analogy Between Extraction and Distillation Distillation Extraction Addition of heat Reboiler Solvent mixer Removal of heat Removal of solvent Condenser Solvent separator Vapor at the boiling point Solvent-rich solution saturated with solvent Superheated vapor Solvent-rich solution containing more solvent than that required Liquid below the boiling point Solvent-lean solution, containing less solvent than that required to saturate it Liquid at the boiling point Solvent-lean solution saturated with solvent Mixture of liquid and vapor Two-phase liquid mixture Relative volatility Relative selectivity Change of pressure Change of temperature D = distillateD = extract product (solute on a solvent-free basis)B = bottomsR = raffinate (solvent-free basis)L =saturated liquid L =saturated raffinate (solvent-free) V = saturated vapor V = saturated extract (solvent-free) A =more volatile component A = solute to be recovered C = less volatile componentC = carrier from which A is extractedF = feedF = feedx =mole fraction A in liquid X = mole or weight ratio of A (solvent-free), A/(A+C)y = mole fraction A in vapor Y = S/(A+C)Chemical Engineering Department | University of Jordan | Amman 11942, Jordan Tel. +962 6 535 5000 | 22888

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### Properties of Extraction Solvents



- The chosen solvent has to meet certain requirements for an efficient extraction
  - Selectivity
  - The solvent should be immiscible or only slightly be miscible with "Feed aqueous phase" to be extracted.
    - The target compound should dissolve very well in the solvent at room temperature ("like dissolves like" rule applies) @ a large difference in solubility leads to a large value for the partition coefficient (also called distribution coefficient), which is important for an efficient extraction
  - Relatively low boiling point (Low vapour pressure) for easy removal at a later stage of the product isolation
  - Chemical reactivity: Stable and inert (non-reactive).

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### Properties of Extraction Solvents



- Recoverability of solute from solvent
  - · No azeotrope formed between solvent and solute
  - · Mixtures should have a high relative volatility
  - · Solvent should have a small latent heat of vapourisation
- A density difference is required between the two phases (densities determine top or bottom)
- Interfacial tension:

The larger the interfacial tension between the two phases the more readily coalescence of emulsions will occur to give two distinct liquid phases but the more difficult will be the dispersion of one liquid in the other to give efficient solute extraction.

 Non-toxic, Low viscosity, Non-flammable (high flash point), cheap, available

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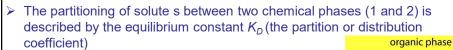
### Solvent miscibility



- Completely miscible
  - Unsuitable for extraction
- Immiscible
  - Ideally suited for extraction
- · Partially miscible
  - Composition dependent
  - Various possibilities
  - Could be used for extraction
- Solubility of organic compounds is a function of the polarities of both the solvent and the solute:
  - "Like Dissolves Like"
  - Polar solvents dissolve polar solutes
  - Nonpolar solvents dissolve nonpolar solutes



#### **Distribution Coefficients**



**A** (in phase 1) 
$$\stackrel{K_D}{\longrightarrow}$$
 **A** (in phase 2)

It is defined as the ratio of concentrations of a solute that is distributed between two immiscible solvents at equilibrium.

$$K_D = \frac{solute\ concentration\ in\ extract\ phase}{solute\ concentration\ in\ raffinate\ phase}$$

$$K_D = \frac{(y_A)_E}{(x_A)_R}$$

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(Phase 2)

(Phase 1)

aqueous phase

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### **Distribution Coefficients**



Ideal condition, when  $K_D >>>> 1$  or <<<<<1

e.g. water - chloroform

Consider a feed of water/acetone(solute).

K = mass fraction acetone in chloroform phase mass fraction acetone in water phase

 $K = \frac{\text{kg acetone/kg chloroform}}{\text{kg acetone/kg water}} = y/x$ 

i.e. acetone is preferentially soluble in the chloroform phase



Distribution Coef	ficients fo	or Immiscible	e Extraction	n	37.500		
	Solute (A)	Solvent	Diluent	<i>T,</i> ° <i>C</i>	$K_d = y_A/x_A$		
$K_{d} = \frac{y_{A}}{x_{A}}$ $K_{d} = \text{distribution coeff.}$ $y_{A} = \text{Solute frac. in Extract}$ $x_{A} = \text{Solute frac. in Raffinate}$	Equilibrium in Weight Fraction Units (Perry and Green, 1984)						
	Acetic acid	Benzene	Water	25	0.0328		
	Acetic acid	Benzene	Water	30	0.0984		
	Acetic acid	Benzene	Water	40	0.1022		
	Acetic acid	Benzene	Water	50	0.0588		
	Acetic acid	Benzene	Water	60	0.0637		
	Acetic acid	1-Butanol	Water	26.7	1.613		
	Furfural	Methylisobutyl ketone	Water	25	7.10		
	Ethyl benzene	β, β'-Thiodipropionitrile	n-Hexane	25	0.100		
	m-Xylene	$\beta$ , $\beta'$ -Thiodipropionitrile	n-Hexane	25	0.050		
	o-Xylene	$\beta$ , $\beta'$ -Thiodipropionitrile	n-Hexane	25	0.150		
	p-Xylene	$\beta$ , $\beta'$ -Thiodipropionitrile	n-Hexane	25	0.080		
	Equilibrium in Mass Ratio Units (Brian, 1972)						
	Linoleic acid (C <sub>17</sub> H <sub>31</sub> COOH)	Heptane	Methylcellosolve + 10 vol % water		2.17		
	Abietic acid (C <sub>19</sub> H <sub>29</sub> COOH)	Heptane	Methylcellosolve + 10 vol % water		1.57		
	Oleic acid	Heptane	Methylcellosolve + 10 vol % water		4.14		
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Dis	Distribution Coefficients for Immiscible Extraction							
	Solute	Organic solvent	K <sub>D</sub> (mol/L) at 25 <sup>o</sup> C					
	Amino acids							
	Glycine	<i>n</i> -butanol	0.01					
	Alanine	<i>n</i> -butanol	0.02					
	2-aminobutyric acid	<i>n</i> -butanol	0.02					
	Lysine	<i>n</i> -butanol	0.20					
	Glutamic acid	<i>n</i> -butanol	0.07					
	Antibiotics							
	Erythromycin	Amyl acetate	120					
	Novobiocin	Butyl acetate	100 at pH 7.0					
		-	0.01 at pH 10.5					
	Penicillin F	Amyl acetate	32 at pH 4.0					
		-	0.06 at pH 6.0					
	Penicillin K	Amyl acetate	12 at pH 4.0					
		-	0.1 at pH 6.0					
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### Example



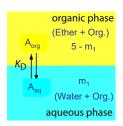
An organic molecule with distribution coefficient (or partition coefficient) of 10 between ether and water, and 150 mL of ether will be used to extract 5.0 g of such organic molecule from 100 mL of water.

Assuming  $m_1$  gram of molecule is left in aqueous phase after the equilibrium is reached, then  $5-m_1$  gram of organic will enter the ether layer. Thus, we have:

$$K_{D} = 10 = \frac{\frac{5.0 - m_{1}}{150} \frac{g}{mL_{ether}}}{\frac{m_{1}}{100} \frac{g}{mL_{water}}} \longrightarrow 10 = \frac{(5.0 - m_{1})(100)}{150m_{1}}$$

$$1500m_1 = 500 - 100m_1 \longrightarrow 1600m_1 = 500$$

$$m_1 = 0.31g$$
  
 $5.0 - m_1 = 5.0 - 0.31 = 4.69g$ 



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# Example Cont.d



After single extraction, only 0.31 g of organic left in water, and 4.69 g is separated from water.

The extraction efficiency = 4.69/5.0 = 93.8%.

#### Example 2

Same amount of ether (150 mL) is used to extract the same organic from 100 mL water but in three portions, each with 50 mL of ether.

Similar calculation can be applied for each cycle of extraction, as follows:

- First cycle of extraction



### Example Cont.d



$$K_{D} = 10 = \frac{\frac{5.0 - m_{1}}{50} \frac{g}{mL_{eiter}}}{\frac{m_{1}}{100} \frac{g}{mL_{water}}}; \quad 10 = \frac{(5.0 - m_{1})(100)}{50m_{1}}$$

$$500m_1 = 500 - 100m_1$$

$$600m_1 = 500$$

$$m_1 = 0.83$$

Hence, 0.83 g of organic remains in aqueous phase, 4.17 g of organic stays in ether

Extraction efficiency = 4.17/5.0 = 83.4%

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# Example Cont.d



2nd Cycle of Extraction

$$K_{D} = 10 = \frac{\frac{0.83 - m_{1}}{50} \frac{g}{mL_{ether}}}{\frac{m_{1}}{100} \frac{g}{mL_{water}}}; \quad 10 = \frac{(0.83 - m_{1})(100)}{50m_{1}}$$

$$500m_1 = 83 - 100m_1$$

$$600m_1 = 83$$

$$m_1 = 0.14$$

- After 2nd cycle of extraction, only 0.14 g of organic is left in aqueous phase, 0.69 g of organic stay in 50 mL of ether.
- 4.86 g of organic is extracted into 100 mL of ether, the extraction efficiency is 4.86/5.0 = 97.2%, already greater than the single extraction (93.8%).



### **Example Cont.d**



3rd Cycle of Extraction

$$K_{D} = 10 = \frac{\frac{0.14 - m_{1}}{50} \frac{g}{mL_{ether}}}{\frac{m_{1}}{100} \frac{g}{mL_{water}}}; \quad 10 = \frac{(0.14 - m_{1})(100)}{50m_{1}}$$

$$500m_1 = 14 - 100m_1$$

$$600m_1 = 14$$

$$m_1 = 0.02$$

- After 3rd cycle of extraction, only 0.02 g of organic remains in aqueous phase, and 4.98 g of organic in total is extracted into 150 mL of ether.
- The extraction efficiency is 4.98/5 = 99.6%.
- If same amount of organic solvent is used for extraction of one molecule, the
  extraction in several portions is much more efficient than single extraction
  using the whole amount of solvent.

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### **Distribution Coefficients**



• In general, using this partition coefficient, one could determine how much of the compound is extracted in each extraction or after *n* extractions:

$$\frac{x}{W_o} = \frac{(Final \ mass \ of \ solute)_{remaining}}{(Initial \ mass \ of \ solute)_{feed}} = \left(\frac{V_{feed}}{V_{feed} + K_D \ V_{Solvent}}\right)'$$

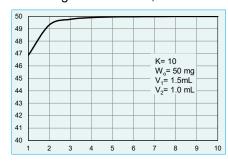
- K<sub>D</sub> = Partition coefficient or distribution coefficient
- V<sub>solvent</sub> = Volume of the organic solvent in each extraction
- V<sub>feed</sub> = Original volume of feed
- n = number of extractions
- W<sub>o</sub> = Initial mass of solute in the feed
- x = Solute remains in aqueous phase

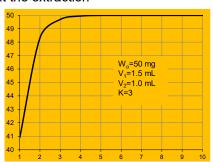
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#### **Distribution Coefficients**



• The larger the K-value, the more efficient the extraction





- For K=10, two extractions are sufficient to extract about 99.6 %.
- For K=3, four extractions are required to accomplish the same degree of the extraction.

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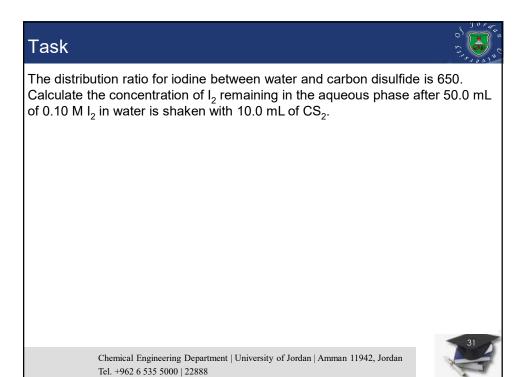
# **Distribution Coefficients**

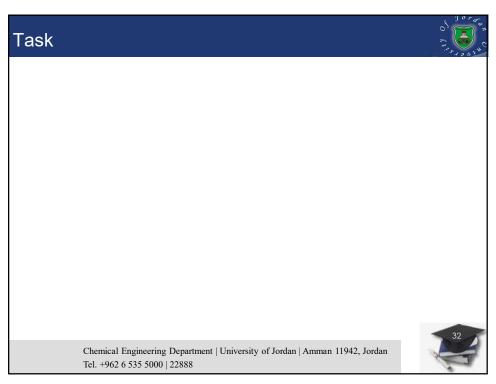


$$\begin{split} K &= \frac{\text{Molarity in organic phase}}{\text{Molarity in aqueous phase}} \\ &\approx \frac{\text{Solubility in organic phase}}{\text{Solubility in aqueous phase}} \end{split}$$

➤ The k value may decrease with increasing the solute concentration in the feed due to the reduction in the solvent extraction capacity







#### **Excursion**



### Liquid-liquid Equilibrium

> The fugacities of species a in each liquid phase are equal:

$$\hat{f}_a^{lpha}=\hat{f}_a^{eta}$$

$$x_a^{\ \alpha} \gamma_a^{\alpha} f_a^{\ \alpha} = x_a^{\ \beta} \gamma_a^{\beta} f_a^{\ \beta}$$

Phase α

> For the same reference state gives:

 $x_a^{\alpha} \gamma_a^{\alpha} f_{\alpha} = x_a^{\beta} \gamma_a^{\beta} f_{\alpha}$ 

Phase β



$$x_a^{\alpha} \gamma_a^{\alpha} = x_a^{\beta} \gamma_a^{\beta}$$

 ${\gamma_a^{\alpha}}$  : Activity coefficient (obtained from Activity coefficient model for  $\mathbf{g^E}$ 

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### Liquid-Liquid Equilibrium



- Two phases:
- Extract
- Raffinate phases
- •Usually three components:
  - Solute (A)
  - Carrier (C)
  - Solvent (S)

(ternary system)



At certain Temperature and pressure

### Liquid-Liquid Equilibrium



➤ The immiscible liquid phases put in contact (the feed and the solvent) form a closed system evolving towards the thermodynamic equilibrium. According to the Gibbs law:

$$F = C - P + 2$$

$$=3-2+2=3$$

- The system can be defined by three parameters (f = 3), the number of components being c = 3, (solvent, solute and carrier), and the phases number P = 2.
- ➤ Usually, the parameters taken into account are the temperature (*T*), the concentration of the solute in the raffinate (*x*) and the concentration in the extract (*y*).
- ➤ So, the equilibrium general equation in this case is:

$$y = f(x)_{t=const}$$





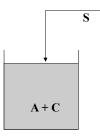
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### Liquid-Liquid Systems



➤ The solvent S is added into the mixture of the diluent C and the solute A, when the system reaches the equilibrium, it

could be homogeneous (i.e. all species are mixed together into a single phase)



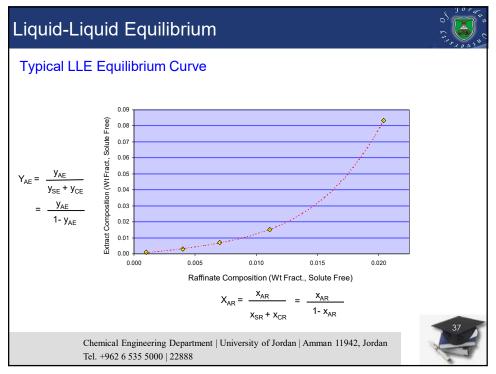
could be divided into 2 phases

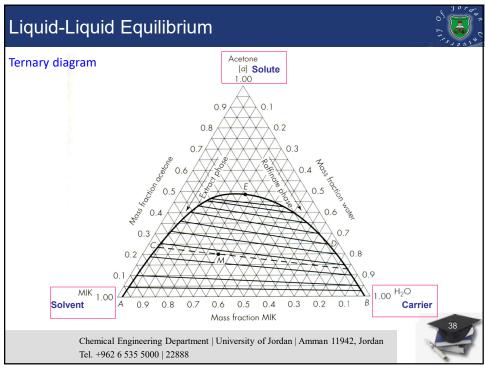
Type III, Type I, Type II

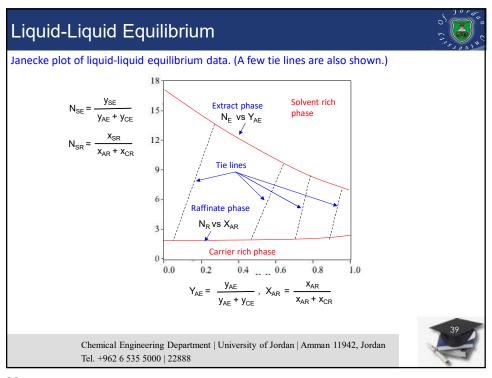
**A + S+** C

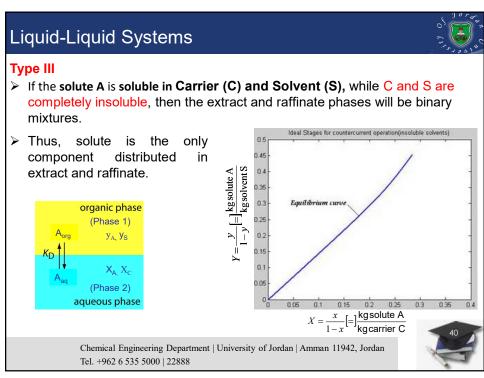
A + C + S











### Liquid-Liquid Systems



- Equilibrium relationship are more complicated 3 or more components present in each phase
  - o Type I: A dissolves completely in S and C, while C and S are only partially miscible
  - Type II: the pairs A and S, S and C, are partially miscible pairs, while A and C are totally soluble

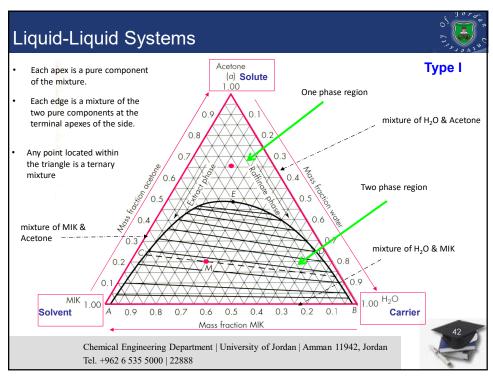
#### Triangular Diagrams

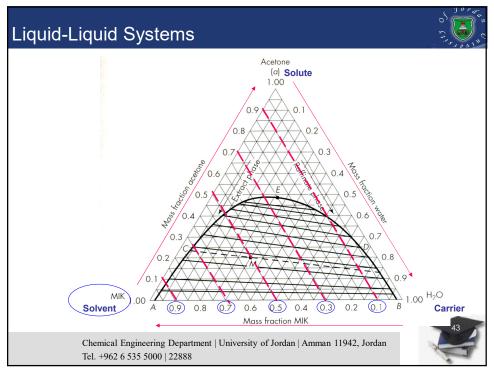
Ternary systems are represented on two types of triangular diagrams:

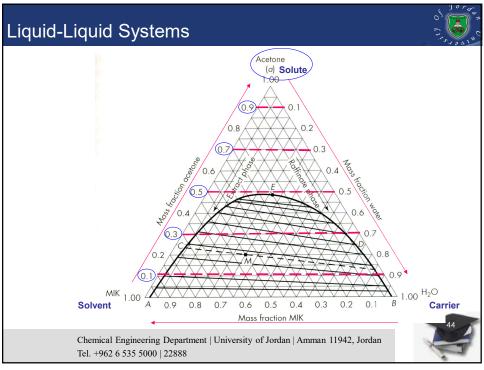
- 1. Equilateral triangles
- 2. Right Triangles
- Assumptions
  - 1) The system is isothermal
  - 2) The system is isobaric
  - 3) The heat of mixing is negligible
  - 4) No chemical reactions

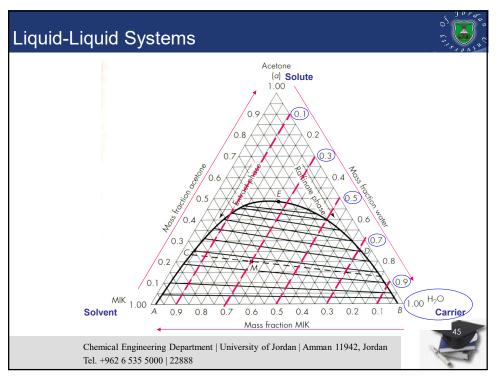
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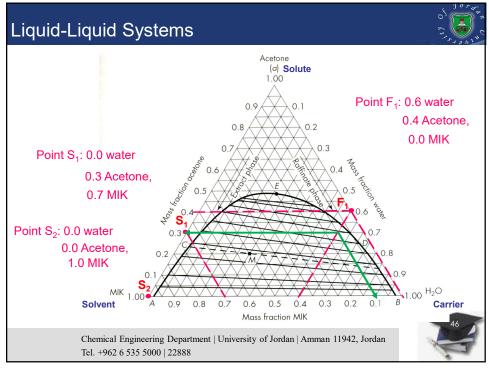


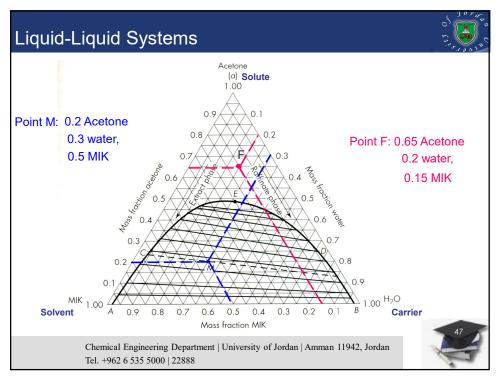


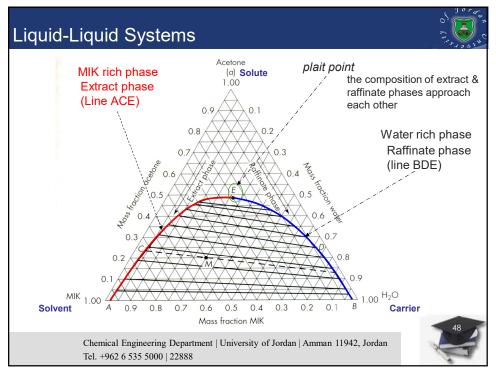


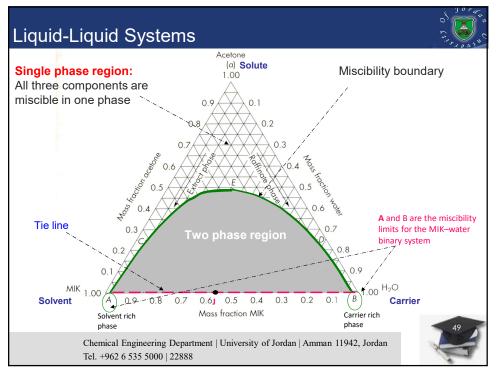


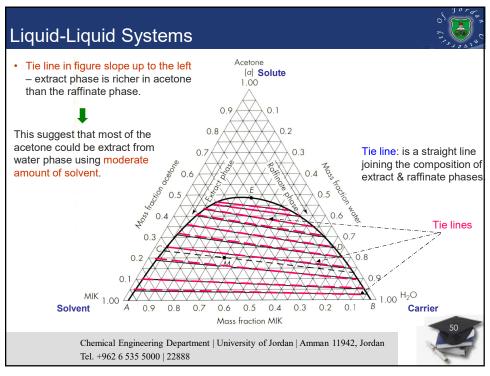


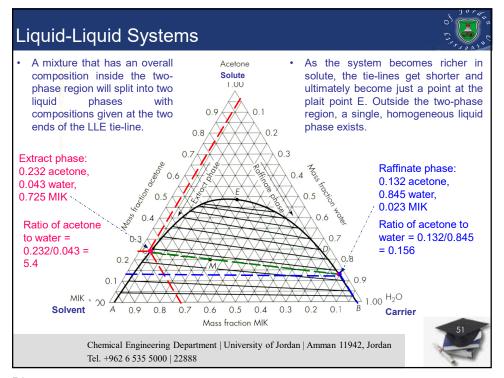


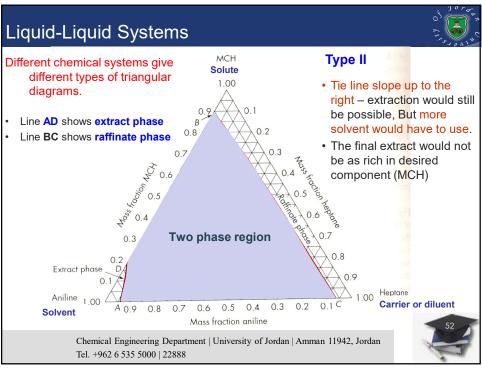


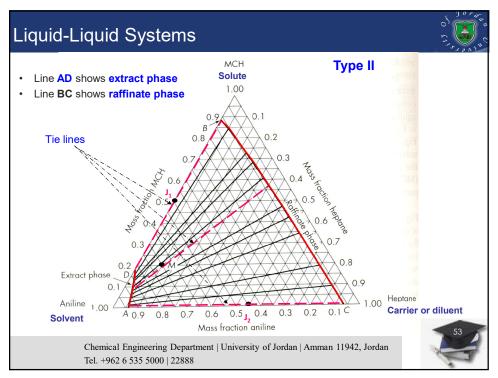


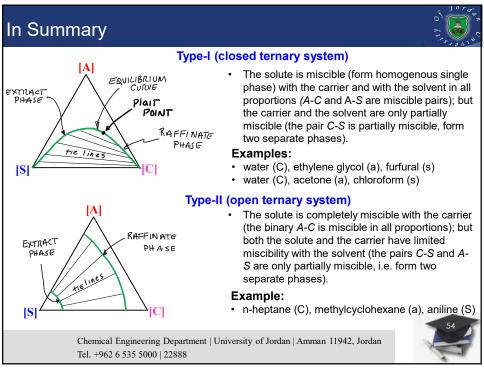


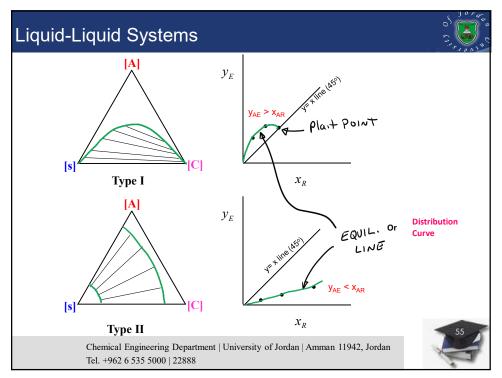


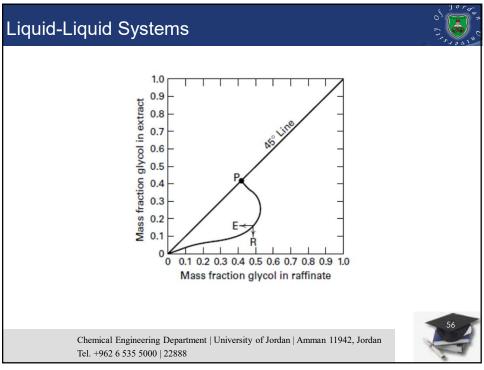


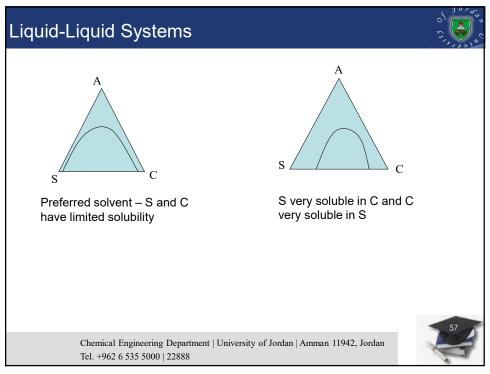


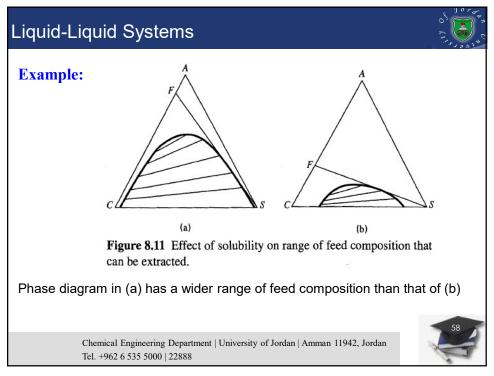


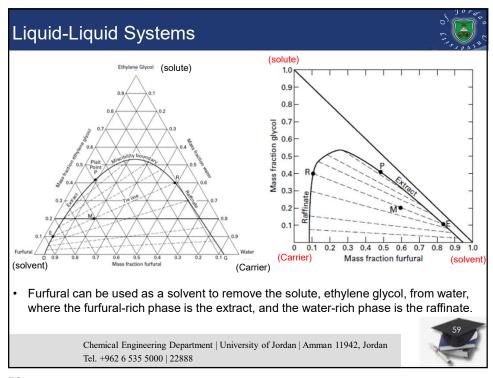


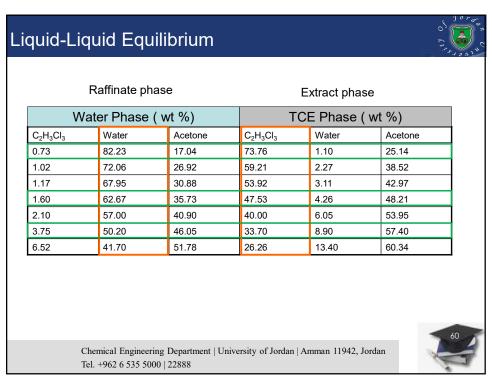


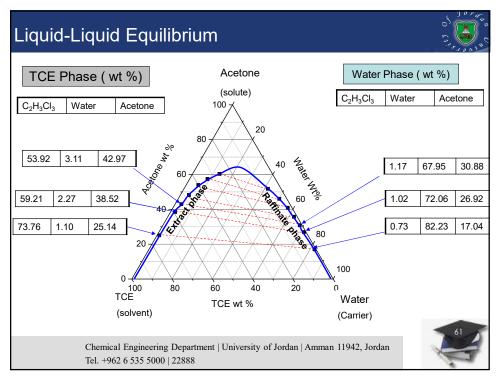


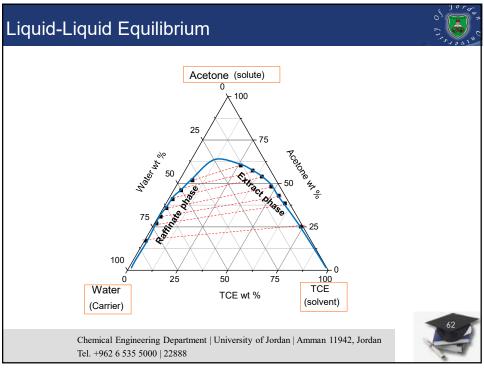


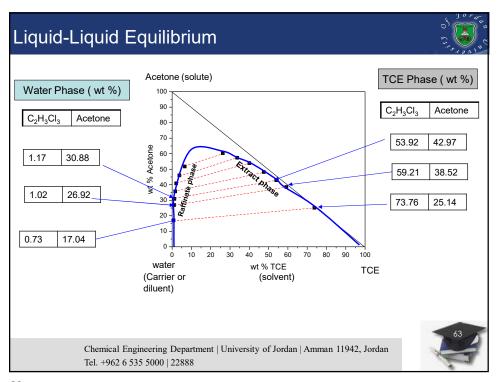


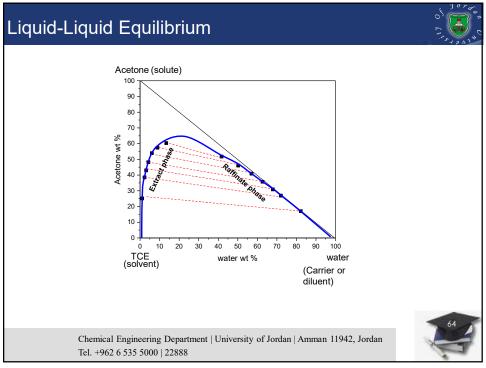


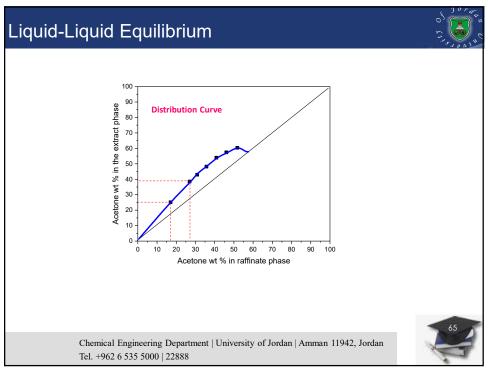


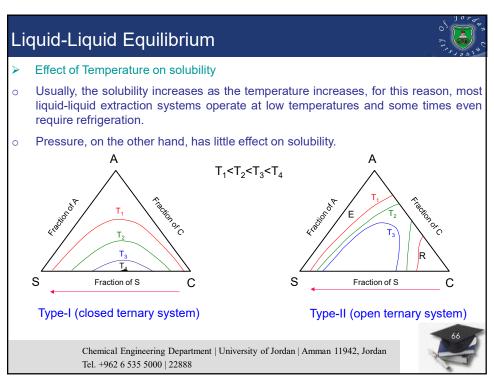












# Single-Stage Equilibrium



Derivation of lever-arm rule for graphical addition

$$\begin{array}{c|c} V, y_A, y_C \\ \hline \\ L, x_A, x_C \end{array}$$

An overall mass balance:

$$V + L = M$$

A balance on A:

$$Vy_A + Lx_A = Mx_{AM}$$

Where  $x_{AM}$  is the mass fraction of A in the M stream.

$$Vy_C + Lx_C = Mx_{CM}$$

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# Single-Stage Equilibrium



Derivation of lever-arm rule for graphical addition

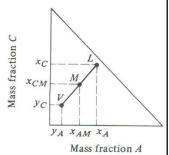
Sub 5.1 into 5.2 
$$\frac{L}{V} = \frac{y_A - x_A}{x_A}$$

$$\frac{L}{V} = \frac{y_C - x_{CM}}{x_{CM} - x_C}$$

Equating 5.4 and 5.5 and rearranging

$$\frac{x_C - x_{CM}}{x_A - x_{AM}} = \frac{x_{CM} - y_C}{x_{AM} - y_A}$$
 (5.6)

Eqn.  $5.6\,$  shows that points L, M, and V must lie on a straight line. By using the properties of similar right triangles,

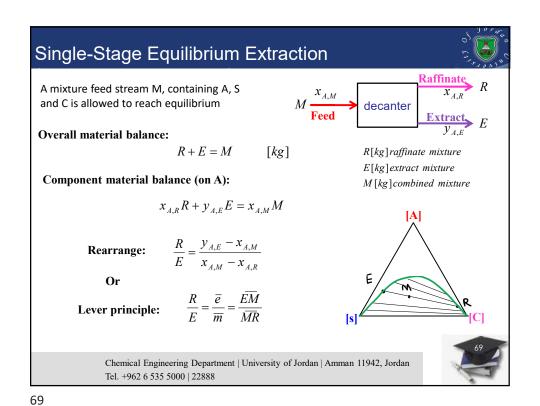


Lever arm's rule

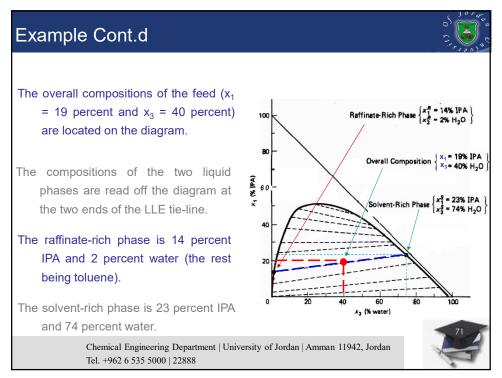
$$\frac{L(kg)}{V(kg)} = \frac{\overline{VM}}{\overline{L}\overline{M}}$$
 (5.7)

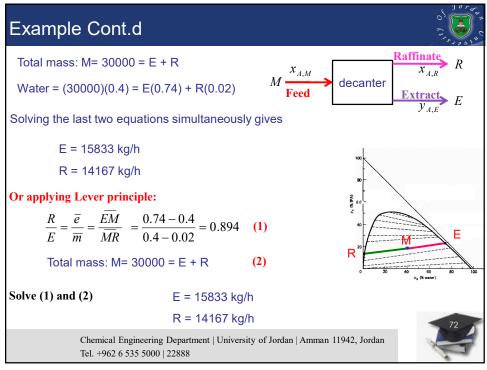
$$\frac{L(kg)}{M(kg)} = \frac{\overline{VM}}{\overline{L}\,\overline{V}} \tag{5.8}$$





Example Extraction of isopropyl alcohol (IPA) from toluene to water Thirty thousand kg/hr of a ternary mixture of: isopropyl alcohol (IPA)  $x_1$ =19 weight percent, toluene  $x_2$  = 41 weight percent, and water  $x_3 = 40$ weight percent are fed into a decanter operating at 25°C. the figure gives the LLE data for the system. Determine the compositions x3 (% water) and flow rates of the two liquid streams leaving the decanter. Chemical Engineering Department | University of Jordan | Amman 11942, Jordan Tel. +962 6 535 5000 | 22888





### Example Cont.d



#### Check the balance for IPA

```
IPA in the Feed = (30000)(0.19) = 5700 \text{ kg/h}

IPA out = S(0.23) + R(0.14)

= (15833)(0.23) + (14167)(0.14) = 5625 \text{ kg/h}
```

The difference is due to the accuracy of reading composition from the diagram

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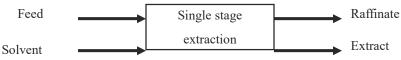
### Operating Modes of Extraction



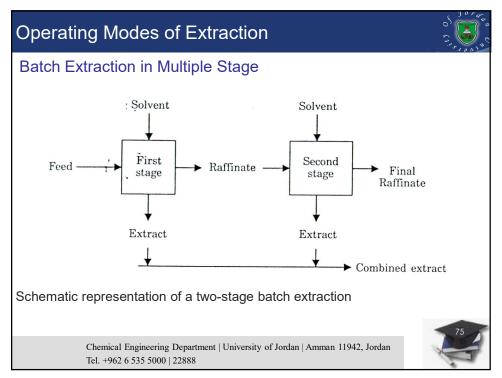
- · Batch or continuous extractions
- · Batch extraction single stage or multiple stage
- Continuous extraction co-current or countercurrent extraction

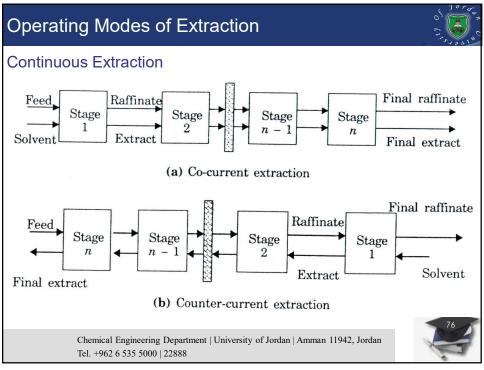
#### **Batch Extraction**

- · The aqueous feed is mixed with the organic solvent
- After equilibration, the extract phase containing the desired solute is separated out for further processing.
- A schematic representation of a single batch operation:







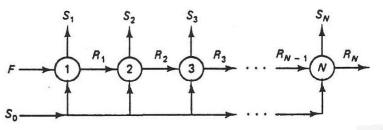


#### **Operating Modes of Extraction**



#### Multiple stages with crossflow of solvent

- If the process liquid stream from the first stages fed into a second extractor and mixed with more fresh solvent, as shown in the Figure, we have what is called cross-flow extraction.
- The process can be described the same as for a single stage .it is simply repeated again for each stage, using the raffinate phase from the upstream stage as the feed to each stage.



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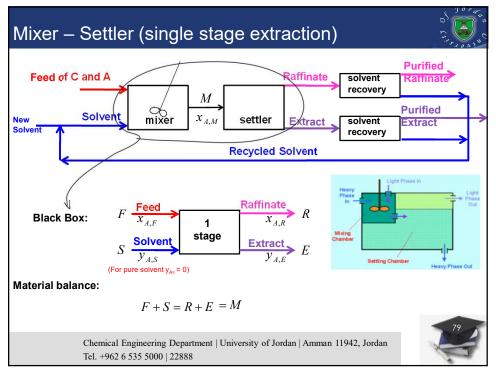
#### **Extraction Equipment**

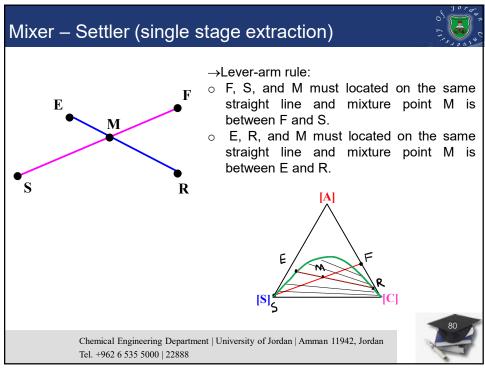


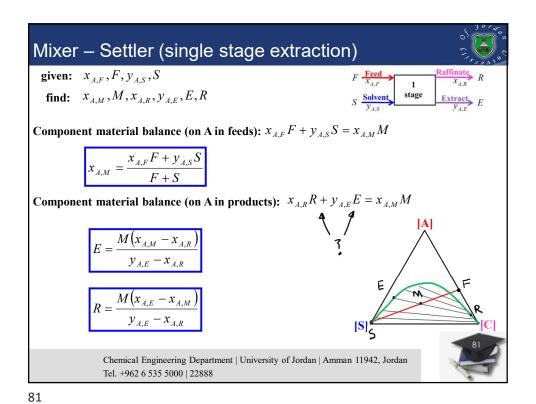
- Extraction Equipments:
  - Mixer settlers
  - Packed extraction towers
  - Perforated plate towers
  - Baffle towers
  - Agitated tower extractors
- Auxiliary equipment:
  - stills, evaporators, heaters and condenser

- Concept of operation: Batchwise or continuous operation
  - Feed liquid + solvent (put in agitated vessel) = layers (to be settled and separated)
  - Extract the layer of solvent + extracted solute
  - Raffinate the layer from which solute has been removed
  - Extract may be lighter or heavier than raffinate.
- Continuous flow more economical for more than one contact process









Mixer — Settler (single stage extraction)  $\frac{R}{E} = \frac{y_A - x_{AM}}{x_{AM} - x_A} = \frac{\overline{EM}}{\overline{RM}}$   $\frac{R}{M} = \frac{y_A - x_{AM}}{y_A - x_A} = \frac{\overline{EM}}{\overline{RE}}$   $\frac{E}{M} = \frac{x_{AM} - x_A}{y_A - x_A} = \frac{\overline{RM}}{\overline{RE}}$ Chemical Engineering Department | University of Jordan | Amman 11942, Jordan Tel. +962 6 535 5000 | 22888



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

[A]

[A]

Extract concentration increases:  $y_{A,E^*} > y_{A,E}$ 

Solute recovery drops:  $x_{A,R^*} > x_{A,R}$ 

Fraction of solute recovered:

$$f = 1 - \frac{(x_{A,R})(R)}{(x_{A,F})(F)}$$

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# Mixer - Settler (single stage extraction)

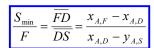
➤ The minimum solvent required for single stage extraction is the quantity when the M point falls at the intersection of the line FS with the Raffinate side of the solubility curve

Minimum Solvent (rate):

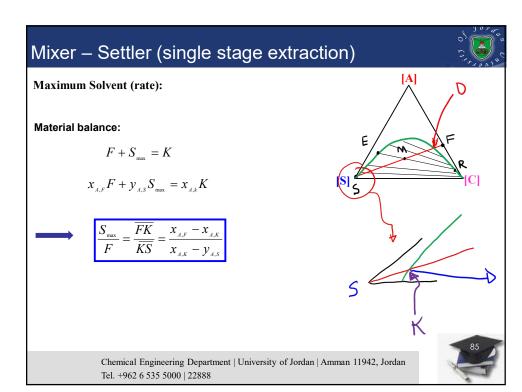
Material balance:

$$F + S_{\min} = D$$

$$x_{AE}F + y_{AE}S_{min} = x_{AD}D$$







### Example

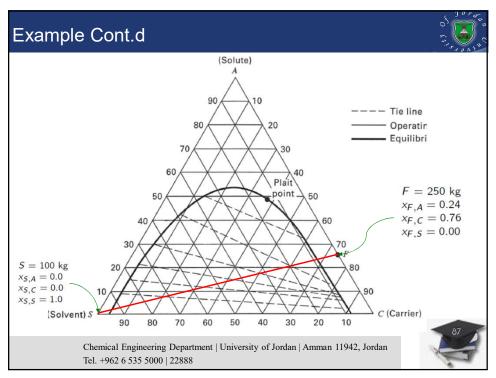


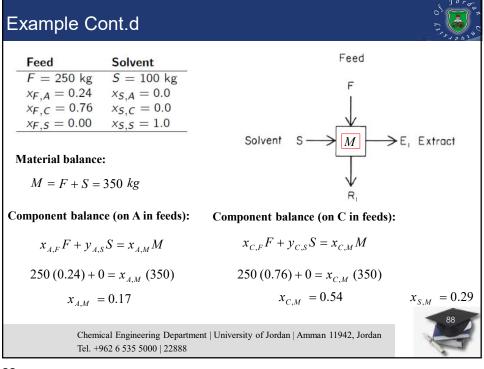
In mixer-settler extraction unit, 250 kg of feed which contains 24 wt% solute (A) 76 wt% carrier(C) is mixed with pure 100 kg solvent (S).

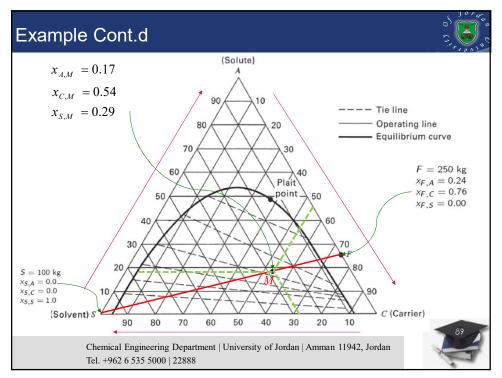
- 1) Find the overall composition of mixture at equilibrium using:
- a) The phase diagram given below
- b) Mass balances
- 2) Find the amounts and compositions of raffinate and extract phases.

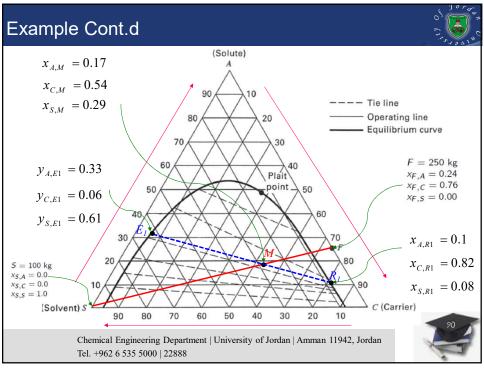
The phase diagram is given on the next slide.

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## Example Cont.d



Material balance:

$$M = R_1 + E_1 = 350 \text{ kg}$$

Component material balance (on A in products):

$$0.1 R_1 + 0.33 E_1 = 350 (0.17)$$

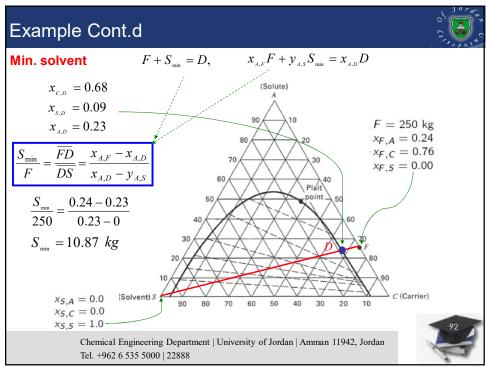
$$R_I = 243.47 \text{ kg}$$
  $E_I = 106.52 \text{ kg}$ 

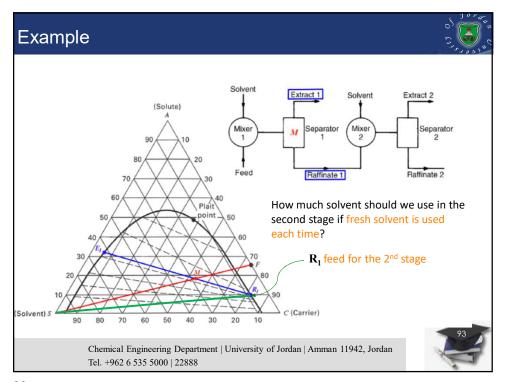
Solute recoverey = 
$$\frac{Fx_{F,A} - Rx_{R,A}}{Fx_{F,A}} = 1 - \frac{Rx_{R,A}}{Fx_{F,A}}$$

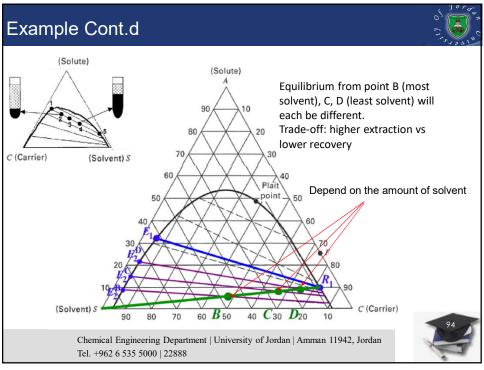
Solute recoverey = 
$$1 - \frac{(243.47)(0.1)}{(250)(0.24)} = 59.4\%$$

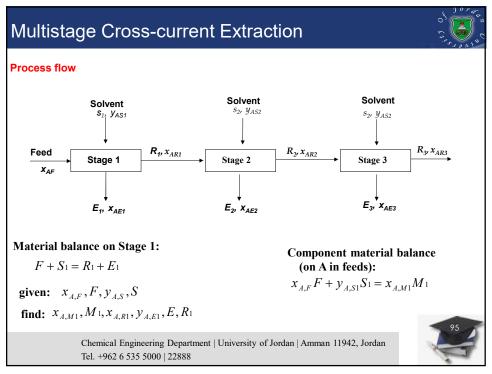
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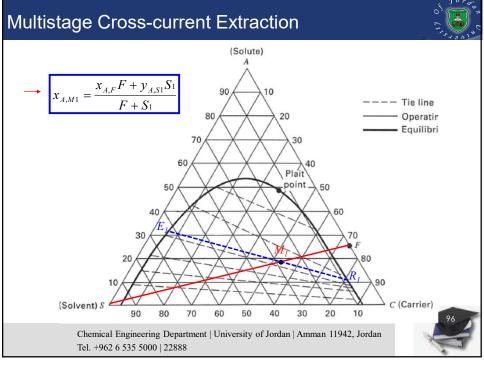












# Multistage Cross-current Extraction



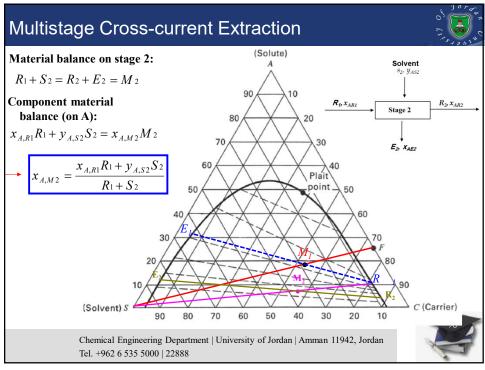
Component material balance (on A in products):  $x_{A,R1}R_1 + y_{A,E1}E_1 = x_{A,M1}M_1$ 

$$E_1 = \frac{M_1(x_{A,M1} - x_{A,R1})}{y_{A,E1} - x_{A,R1}}$$

$$R_1 = \frac{M(x_{A,E1} - x_{A,M1})}{y_{A,E1} - x_{A,R1}}$$

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# Multistage Cross-current Extraction



Component material balance (on A in products):

$$x_{A,R2}R_2 + y_{A,E2}E_2 = x_{A,M2}M_2$$

$$E_2 = \frac{M_2(x_{A,M2} - x_{A,R2})}{y_{A,E2} - x_{A,R2}}$$

$$R_2 = \frac{M(x_{A,E2} - x_{A,M2})}{y_{A,E2} - x_{A,R2}}$$

In similar Manner you can obtain the relations for Stage 3

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# Multistage Cross-current Extraction



Recovery≡ fraction of solute recovered

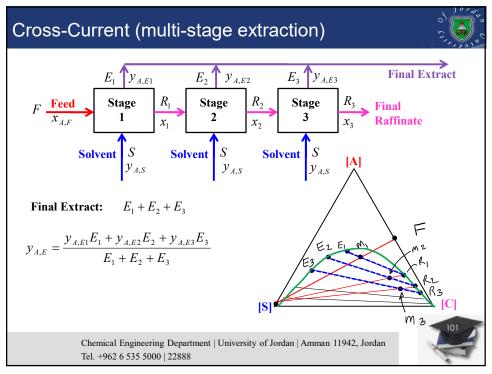
Solute recovery = 
$$1 - \frac{R_N x_{R_N,A}}{F x_{F,A}}$$

N: number of stages

Overall solute concentration in the extract

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



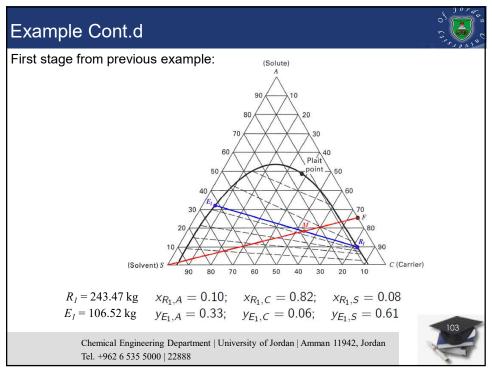


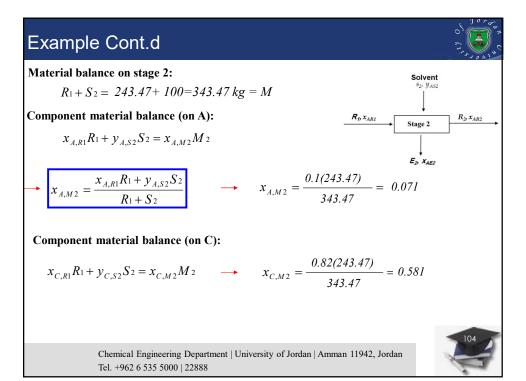
#### Example

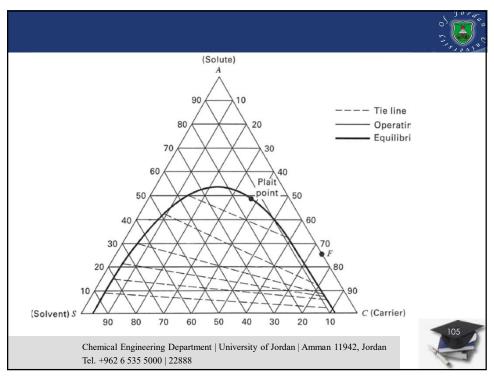


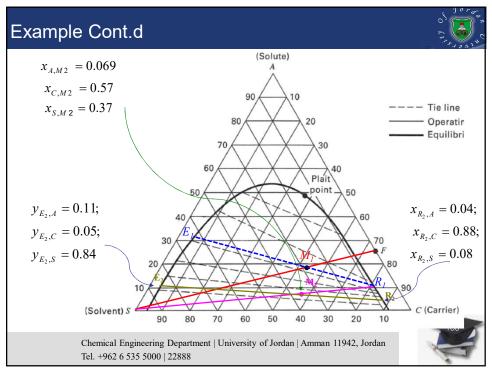
Cross-current mixer-settler extraction units are used for extraction process of 250 kg of feed which contains 24 wt% solute (A) and 76 wt% carrier(C). Each stage is supplied with pure 100 kg solvent (S). Find the minimum number of stages required to achieve at least 85% solute recovery. Find the corresponding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











#### Example Cont.d



Component material balance (on A in products):  $x_{A,R2}R_2 + y_{A,E2}E_2 = x_{A,M2}M_2$ 

$$E_2 = \frac{M_2(x_{A,M2} - x_{A,R2})}{y_{A,E2} - x_{A,R2}} \longrightarrow E_2 = \frac{343.47(0.069 - 0.04)}{0.11 - 0.04} = 142.29 \text{ kg}$$

$$M_2 = R_2 + E_2$$
  $R_2 = M_2 - E_2 = 343.47 - 142.29 = 201.17 kg$ 

Solute recoverey = 
$$1 - \frac{R_2 x_{R_2,A}}{F x_{F,A}} = 1 - \frac{201.17(0.04)}{(250)(0.24)} = 86.5 \% > 0.85 (required)$$

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

Overall solute concentration:

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

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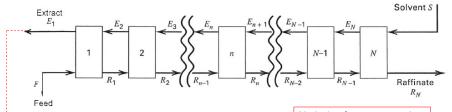


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# Continuous Multistage Countercurrent Extraction



#### N units in counter-current arrangement:



N: index for stage number

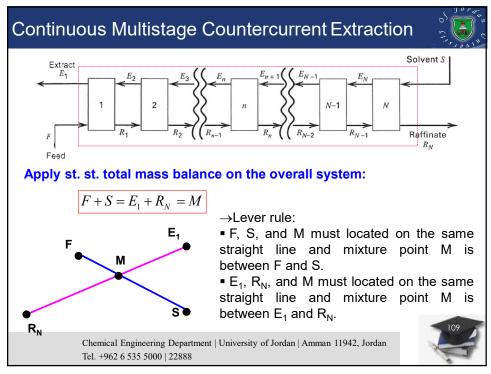
- "Re-use" of solvent
- E<sub>n</sub> and R<sub>n</sub> for n=1,...N leaving each stage are in equilibrium [they are determined via the tie line]
- Solute Recovery:

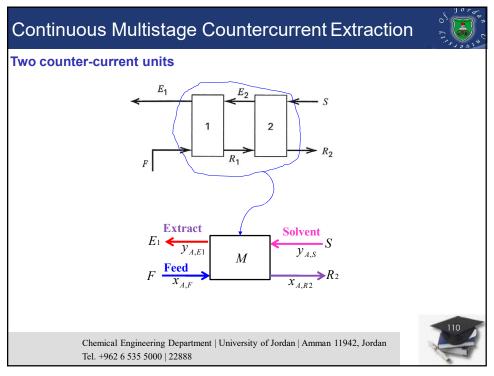
Solute recovery = 
$$1 - \frac{R_N x_{R_N,A}}{F x_{F,A}}$$

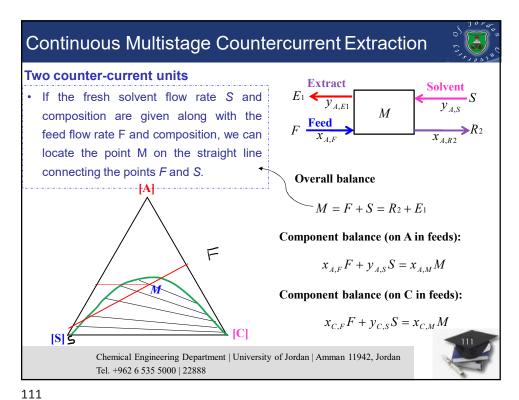
• Overall solute concentration:  $\overline{v}_{n,j}$ 

$$\overline{y}_{E,A} = y_{E_1,A}$$

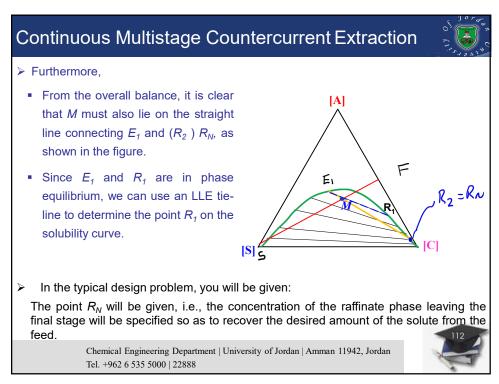


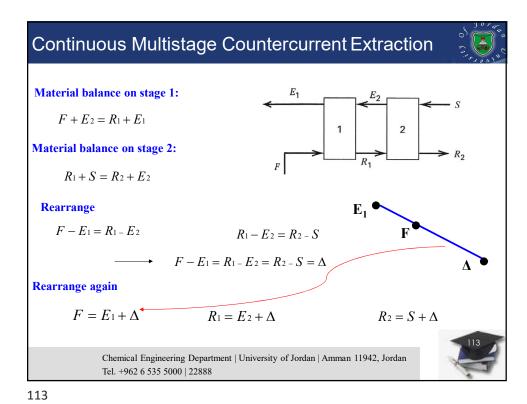






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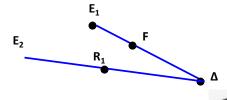


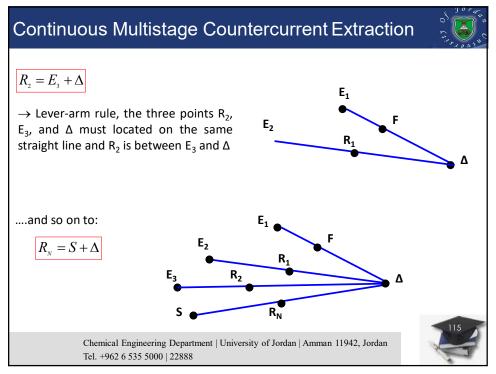
# Continuous Multistage Countercurrent Extraction

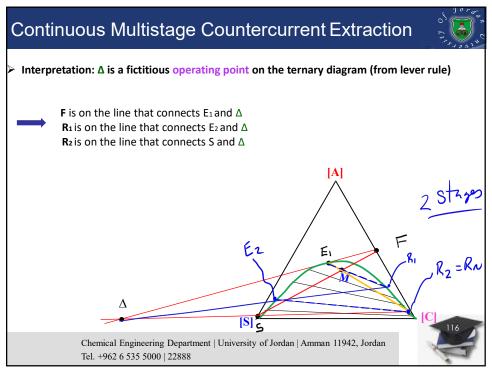
37.7.1.1

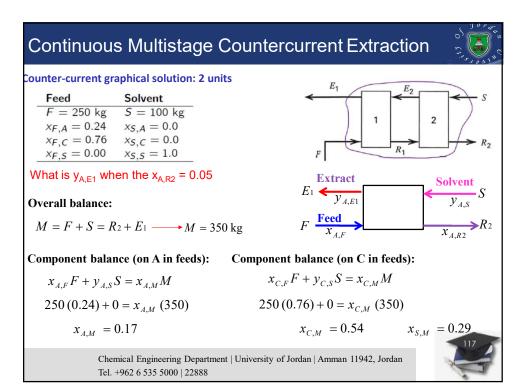
- $\circ$   $\Delta$ : a pseudo flow rate with pseudo compositions  $x_{\wedge}$
- $_{\odot}$  This fictitious  $_{\Delta}$  stream serves the same purpose as the operating lines did in binary distillation.
- It provides a graphical way to solve the mass balances that describe this ternary system simultaneously:

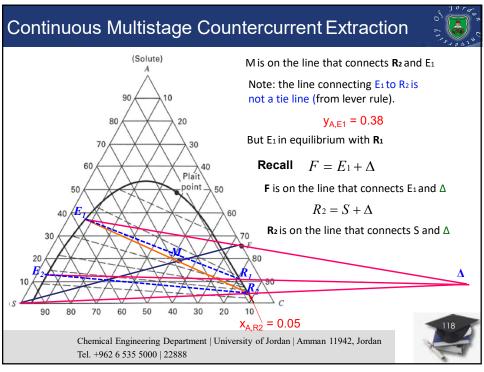
 $R_1 = E_2 + \Delta$   $\rightarrow$  Lever-arm rule, the three points  $R_1$ ,  $E_2$ , and  $\Delta$  must located on the same straight line and  $R_1$  is between  $E_2$  and  $\Delta$ 

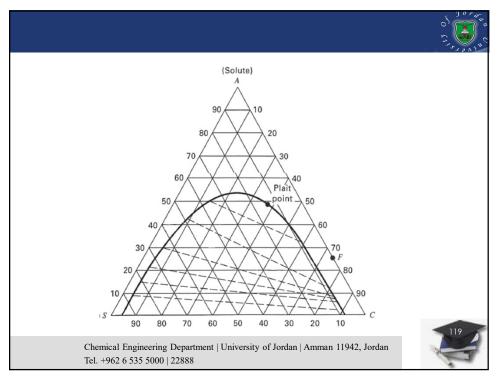


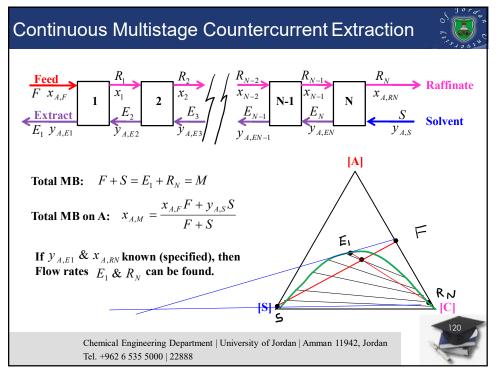












### Continuous Multistage Countercurrent Extraction



Material balance:

$$F + E_2 = R_1 + E_1$$

$$R_2 + E_2 = R_1 + E_3$$

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

Rearrange

$$F - E_1 = R_1 - E_2$$

$$R_1 - E_2 = R_2 - E_3$$

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

$$F - E_1 = R_1 - E_2 = \dots = R_{n-1} - E_n = \dots = R_{N-1} - S = \Delta$$

Notes

- 1. each difference is equal to  $\Delta$  (the difference between flows)
- 2. En and Rn are in equilibrium, leaving each stage [via tie line]

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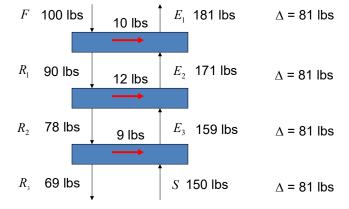
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# Continuous Multistage Countercurrent Extraction



# ∆ point



$$F - E_1 = R_1 - E_2 = \dots = R_{n-1} - E_n = \dots = R_N - S = \Delta$$



### Continuous Multistage Countercurrent Extraction



- We know F and S; Connect S and F points with a line.
- Locate the mixture point M using overall mass balance and lever rule.
- 3. Either specify E<sub>1</sub> or R<sub>N</sub> (we will always know one of them)
- 4. Connect a straight line through M passing through the one specified
- 5. Solve for unspecified one [via tie line]

- 6. Connect S through RN and extrapolate
- 7. Connect E<sub>1</sub>through F and extrapolate; cross lines at Δ
- 8. Locate △ by intersection of 2 lines
- 9. In general: connect Enand Rnvia equilibrium tie lines.
- 10. Repeat until reaching R<sub>N</sub>



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#### Example

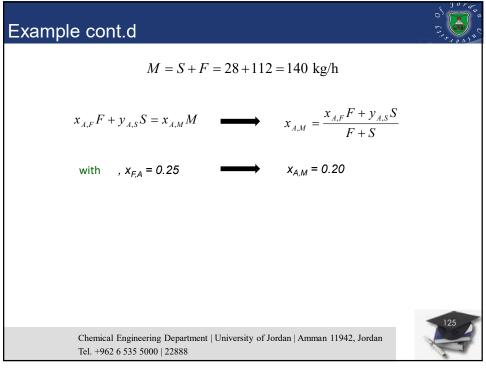


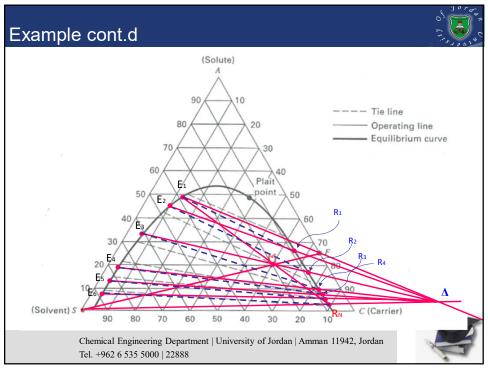
**Example.** Consider a system for which you have been given the ternary diagram . A = solute, S = solvent (100% pure), C = carrier. In a counter-current extraction process, the feed, F enters at 112 kg/hr with composition of 25 wt% solute and 75 wt% carrier. The solvent flow rate is 28 kg/hr.

- 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.

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

The objective now is to have a counter-current system so the raffinate leaving in the  $N_{th}$  stage,  $R_N$  has  $y_{A,RN}$  = 0.025





# Example cont.d

3,5100

**Total MB:**  $F + S = E_1 + R_N = M = 140$ 

 $x_{R_1,A} = 27.3\%$ 

From the diagram,

 $y_{E_{2,A}} = 45\%$ 

**Total MB on A:**  $x_{A,M}M = y_{A,E1}E_1 + x_{A,RN}R_N$ 

 $x_{R_2,A} = 17.3\%$  $y_{E_3,A} = 34\%$ 

From the diagram,

 $x_{R_2,A} = 10\%$ 

$$x_{R_{\rm M},A} = 0.025$$
  $y_{E_{\rm I},A} = 48\%$  also  $x_{\rm A,M} = 0.25$ 

 $y_{E_4,A} = 20\%$ 

$$\rightarrow E_1 = 53.48 \, kg/h$$
 and  $R_N = 86.15 \, kg/h$ 

 $x_{R_4,A} = 6.0\%$  $y_{E_5,A} = 12.5\%$ 

Remember that

 $x_{R_5,A} = 4.0\%$ 

$$F - E_1 = R_1 - E_2 = \dots = R_{n-1} - E_n = \dots = R_{N-1} - S = \Delta$$

$$y_{E_6,A} = 7.0\%$$

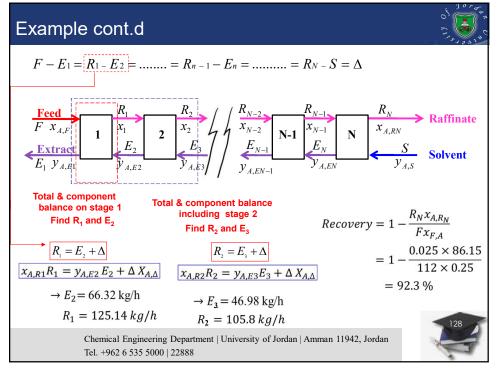
$$\rightarrow \Delta = F - E_1 = 112 - 53.48 = 58.82 \, kg/h$$

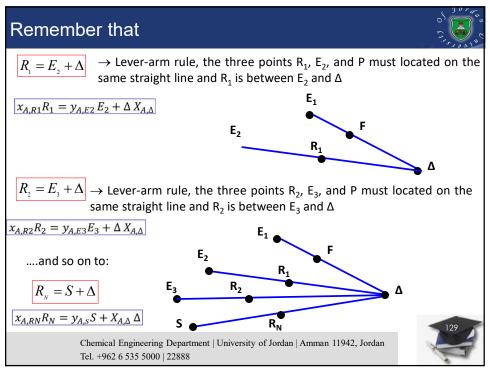
 $x_{R_6,A} = 1.5\%$ 

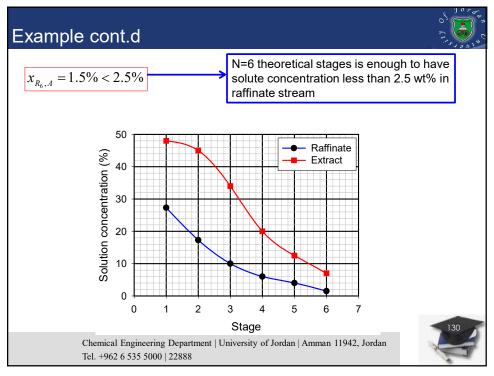
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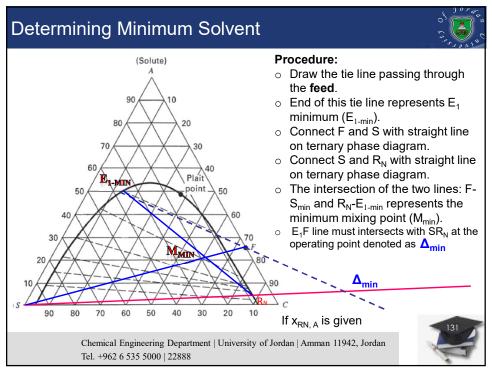
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### **Determining Minimum Solvent**



Using these fractions, do mass balance to calculate S<sub>min</sub>

The material balances can be established as follows

$$F + S \min = M \min = R_N + E_1$$

$$x_{A,F}F + x_{A,S}S$$
 min  $= x_{A,M}M$  min

$$x_{A,F}F + x_{A,S}S \min = x_{A,M}(F + S \min)$$

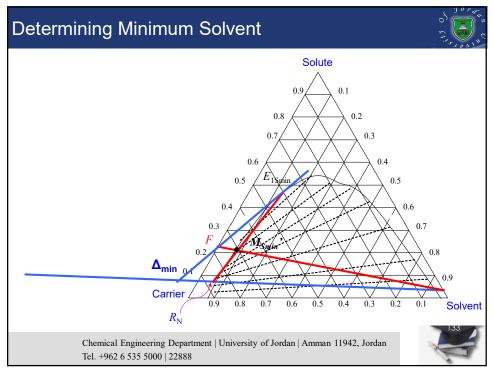
$$\frac{S_{\min}}{F} = \frac{x_{A,F} - x_{A,M}}{x_{A,M} - y_{A,S}}$$

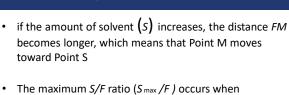
• The optimal operating S/F is approximately 1.5 S min /F

In the previous figure, calculate S<sub>min</sub>/F

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







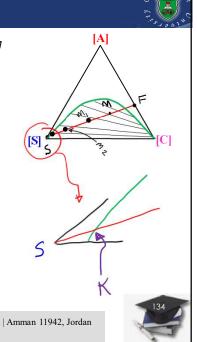
**Determining Maximum Solvent** 

$$\frac{S_{Max}}{F} = \frac{x_{A,F} - (x_{A,M})_{Max}}{(x_{A,M})_{Max} - y_{A,S}}$$

Point M reaches the extract-phase curve,

When Point M is on the *extract-phase* curve, no raffinate phase is formed, and only a single stage is needed, which is impractical

**Remark.** With  $S_{max}/F$ , the required number of theoretical stages:  $N\rightarrow 1$ 



### **Determining Maximum Solvent**



- 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 :  $S \approx 1.5 S_{\min}$

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#### Counter-current stage extraction with immiscible liquids

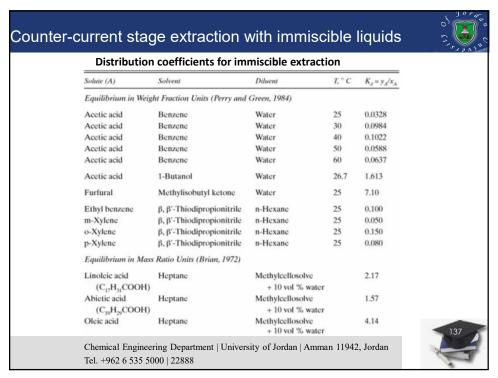


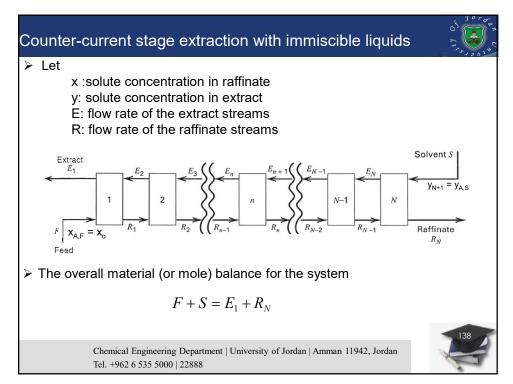
- The carries (C) of solute (A) is immiscible in solvent (S).
- In other words, solute is the only component distributed in extract and
- > This means that the raffinate has a binary mixture of A and C and the extract has binary mixture of A and S.
- In such ternary coordinates is not helpful.
- > As in distillation and absorption, the equilibrium xy diagram is used
- > Equilibrium data for dilute extraction are usually represented as a distribution ratio, K<sub>d</sub>

$$K_D = \frac{(y_A)_E}{(x_A)_R}$$

 $K_D = \frac{(y_A)_E}{(x_A)_R}$  (g A/g extract)/(g A/g raffinate) (mol A/mol extract)/(mol A/mol raffinate)







#### Counter-current stage extraction with immiscible liquids



> The material (or mole) balance for species A of the system

$$x_{A,F}F + y_{A,S}S = y_{A,E1}E_1 + x_{A,RN}R_N$$

➤ Let

X :solute to carrier ratio in raffinate

Y: solute to solvent ratio in extract

E': flow rate of solvent in the extract streams

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

$$R_0' = F(1-x_{AF}) = R(1-x)$$

$$E' = S (1-y_{N+1}) = E (1-y)$$

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#### Counter-current stage extraction with immiscible liquids



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

$$X = \frac{x}{1 - x} [=] \frac{\text{kg solute A}}{\text{kg carrier C}}$$

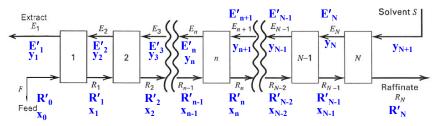
•and solute-to-solvent mass ratio in the extract:

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

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#### Counter-current stage extraction with immiscible liquids





■ 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:  $y_{N+1} = 0 \Rightarrow E' = S$ 

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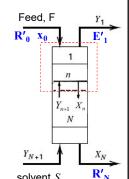
#### Counter-current stage extraction with immiscible liquids



■ Applying mass balance for solute A over stages: 1→N:

$$R'\left(\frac{x_{0}}{1-x_{0}}\right) + E'\left(\frac{y_{N+1}}{1-y_{N+1}}\right) = R'\left(\frac{x_{N}}{1-x_{N}}\right) + E'\left(\frac{y_{1}}{1-y_{1}}\right)$$

$$E'Y_{N+1} = R'X_{N} + E'Y_{1} - R'X_{0}$$



■ Applying mass balance for solute A over stages: 1→n:

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

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



#### Counter-current stage extraction with immiscible liquids



$$ightarrow$$
 Dividing by E' gives:  $Y_{n+1} = \frac{R'}{E'} X_n + Y_1 - \frac{R'}{E'} X_0$  Operating line equation

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

Slope = 
$$\frac{R'}{E'}$$

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

 $\bullet$  For certain feed flow rate, the minimum solvent flow rate,  $\mathbf{S}_{\min}$  must correspond to the maximum allowable slope:

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

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

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#### 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	У
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) = Nicotine; Carrier (B) = Water
 Solvent (S) = Kerosene

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

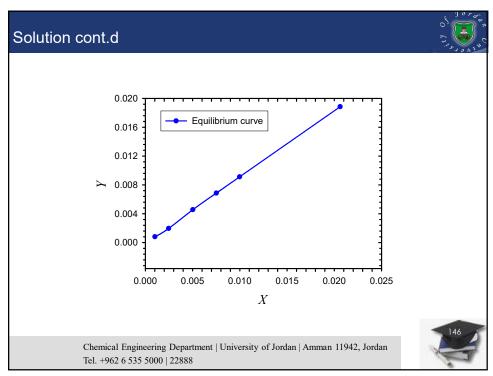
•Re-describe the equilibrium data in terms of solute-to-carrier mass ratio (X) and solute-to-solvent mass ratio in the raffinate

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

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#### Solution cont.d



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

- 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:

$$X_0 = x_0 / (1 - x_0) = 0.01$$
  
 $X_N = x_N / (1 - x_N) = 0.001$ 

 $Y_{N+1} = y_{N+1} / (1 - y_{N+1}) = 0.0005$ 



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#### Solution cont.d



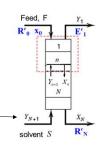
5. Determine  $Y_1$ . The point  $(X_N, Y_{N+1}) = (0.001, 0.0005)$  must lies on the operating line, thus

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

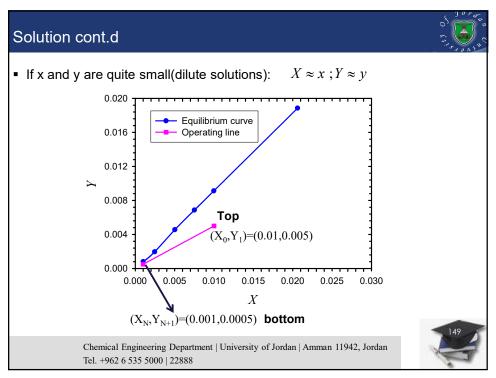
$$0.0005 = (0.50)(0.001) + Y_1 - (0.50)(0.01) \rightarrow Y_1 = 0.005$$

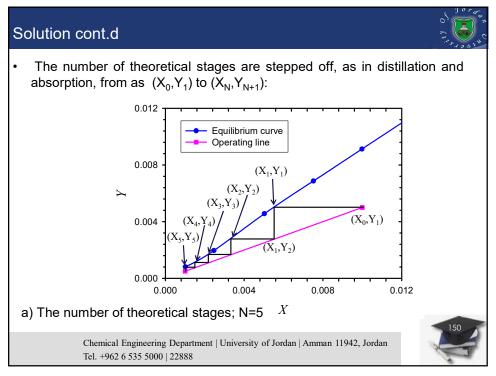
The point  $(X_0,Y_1)=(0.01,0.005)$  must also must lies on the operating line.

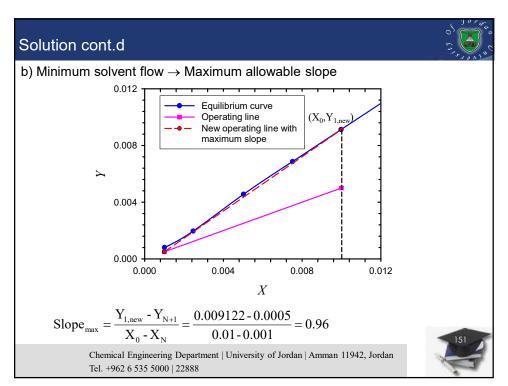
6. With the two point:  $(X_N, Y_{N+1}) = (0.001, 0.0005)$  and  $(X_0, Y_1) = (0.01, 0.005)$  we can now draw the operating line.











#### Solution cont.d



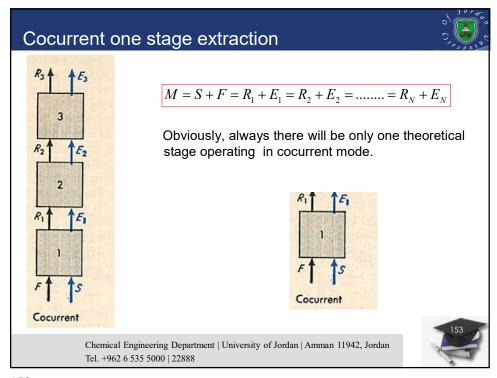
b) Minimum solvent flow  $\rightarrow$  Maximum allowable slope

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

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

• 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.

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#### 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:

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

Where H is the height of extraction tower



