CE407 SEPARATIONS

Lecture 14

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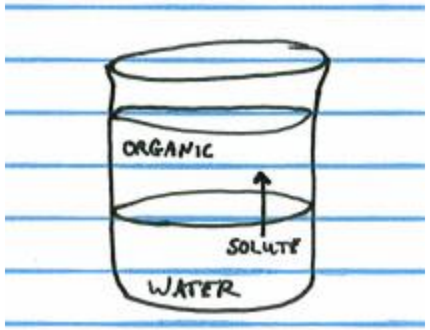
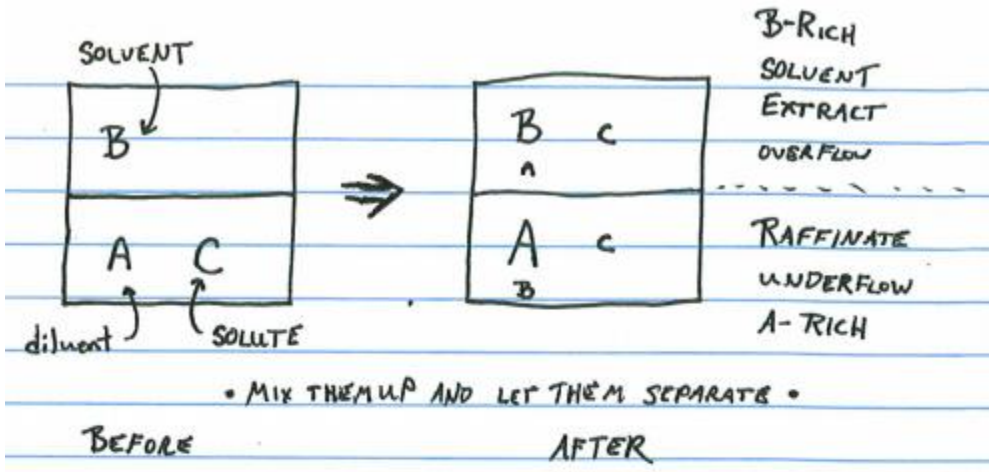
Liquid Liquid Extraction McSH pp772-791 Treybal pp 433-453

- In some cases, a solute in a liquid solution may prove difficult to separate via distillation
  - Perhaps the relative volatilities are close together
  - Perhaps there are suspended solids
- The addition of another liquid solvent which is immiscible with the first solvent and in which the solute prefers to dissolve can extract the solute into the new solvent
- We now have the solute dissolved in a new solvent
  - It STILL needs to be separated
  - But, if the new solution is easier to separate than the first one was we have still made progress…



Liquid Liquid Extraction



- Start with solute, C, dissolved in the diluent, A
- Add solvent, B
- A and B do not mix
  - Some A does dissolve in B
  - Some B does dissolve in A
- Mix them well and then let the two phases separate
- We would undertake this if B and C are easier to separate than A and C
- The phase that is rich in **solvent** B is called **Extract**
- The phase that is rich in **diluent** A is called **Raffinate**
- Solvent B must have a favorable affinity for the solute C in order for this to work
  - That's science talk for: C should prefer to dissolve in B compared to dissolving in A

Liquid Liquid Extraction

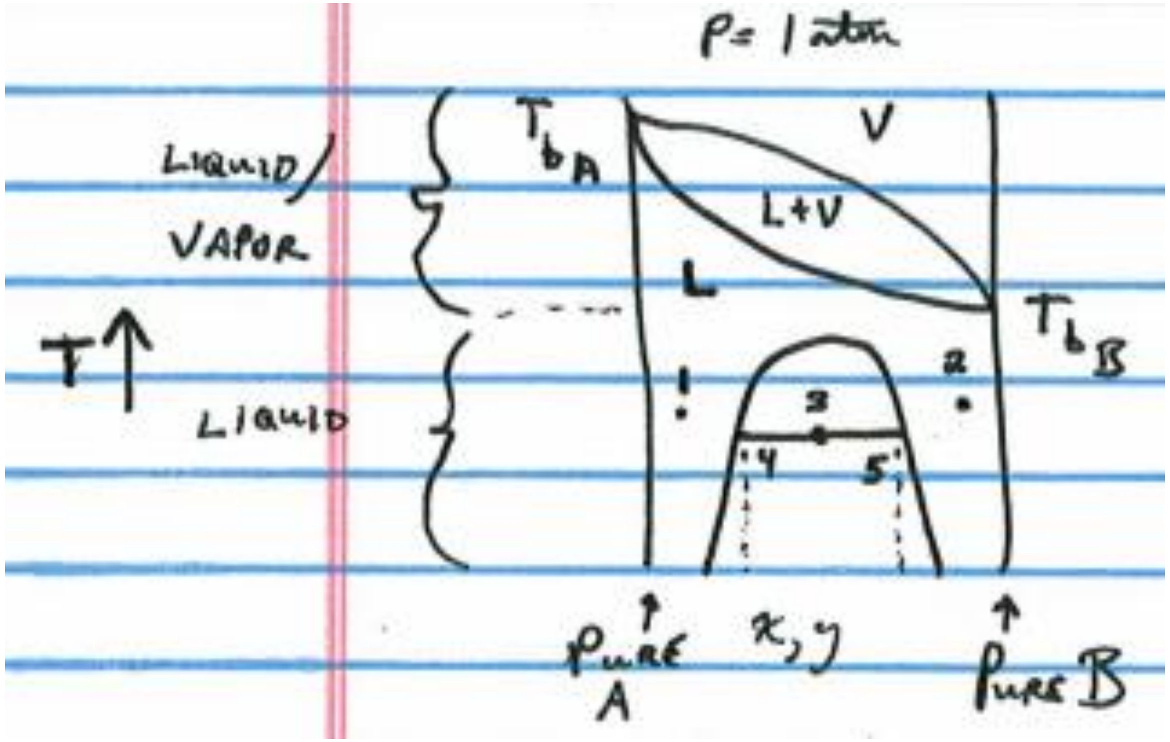
- Good Candidates for LLE
  - Original solution is “Dirty” with solids or other chemicals
  - Dilute aqueous solutions will require very high amounts of energy to distill
  - A and C have similar boiling points

Liquid Liquid Extraction – Phase Diagrams

- Binary diagram – we have already encountered the liquid/vapor section
- Notice that the phase behavior depends on the temperature

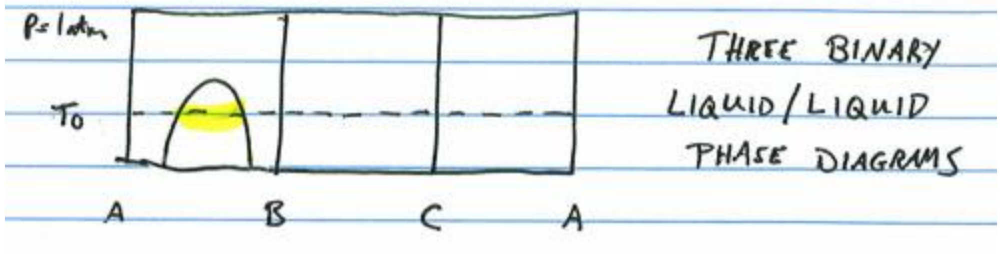
1) A with a small amount of B added – One Phase
2) B with a small amount of A added – One Phase
3) Large amount of both A and B added together will separate into two phases
    4) Raffinate
    5) Extract

- Any point within the Two Phase Bubble will separate across a Tie Line to composition indicated at the boundary of the two phase region
- For a binary mixture the tie line is horizontal

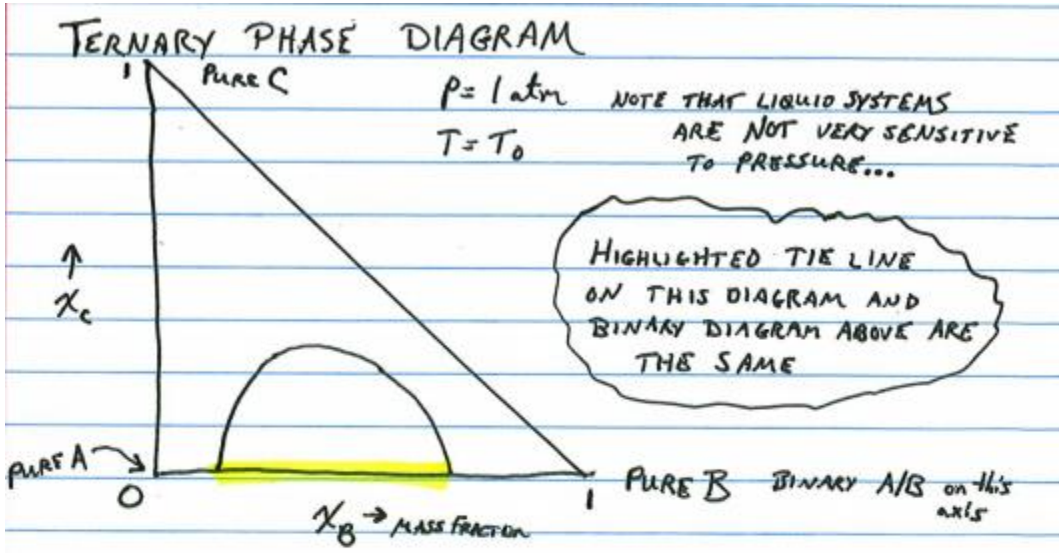


Note:
- VLE always uses MOLE fractions
- Liquid Liquid usually uses MASS fractions
- For the LLE part of the course it will be understood that we are dealing in MASS fractions

Liquid Liquid Extraction – Phase Diagrams

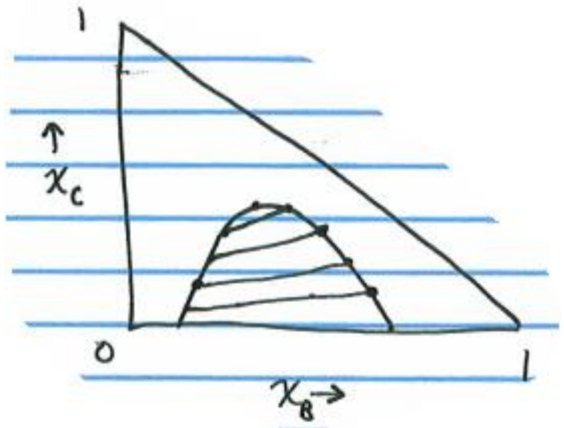


- Represented as three binary pairs
  - B and C are totally miscible, no phase boundary exists
  - Same for A and C



- **Ternary Phase Diagram**
  - This diagram has mass fractions $\mathbf{x_B}$ and $\mathbf{x_C}$ as axes
  - Because $\mathbf{x_A = 1 - x_B - x_C}$ all three mass fractions are determined by any point on the diagram
  - The three corners represent the three components in pure form
  - Highlighted yellow line is the same tie line on both diagrams

Liquid Liquid Extraction – Phase Diagrams



- Only reliable source of information for this data is experimental
- Create mixtures of various compositions, mix, and let equilibrate, then measure the compositions of each phase
- Generates phase boundary and tie lines
- A diagram will be good for one temperature and pressure
  - Liquid phase diagrams are not very sensitive to pressure changes
- At different temperatures the shape of the boundary and the slopes of the tie lines will change
  - The slope of the different tie lines on a graph may be different

Raffinate		Extract	
x_B	x_C	x_B	x_C
~	~	~	~
~	~	~	~

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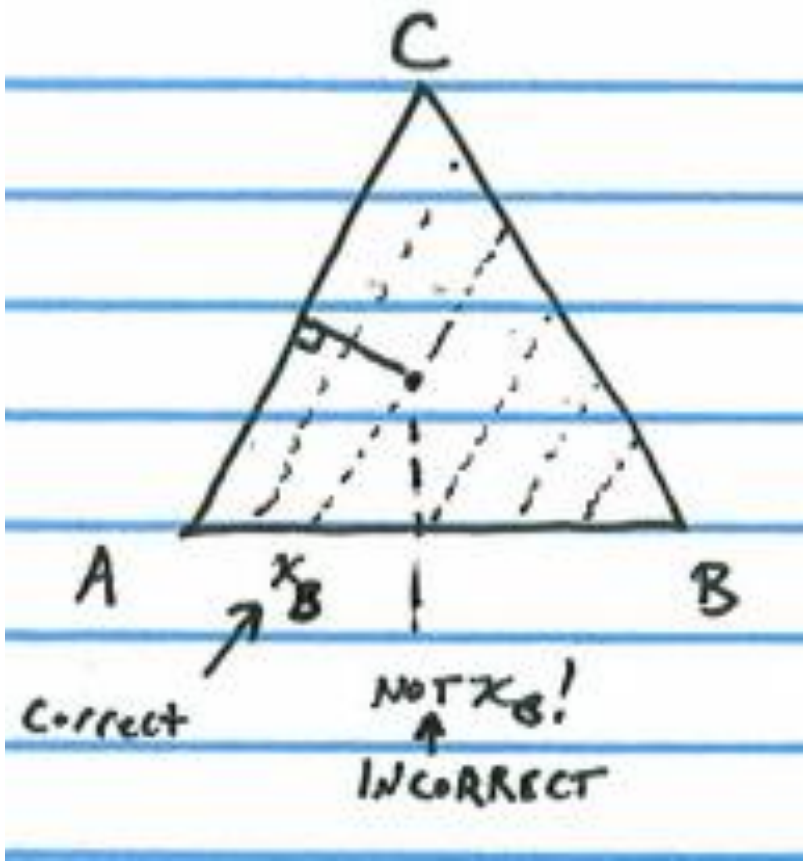
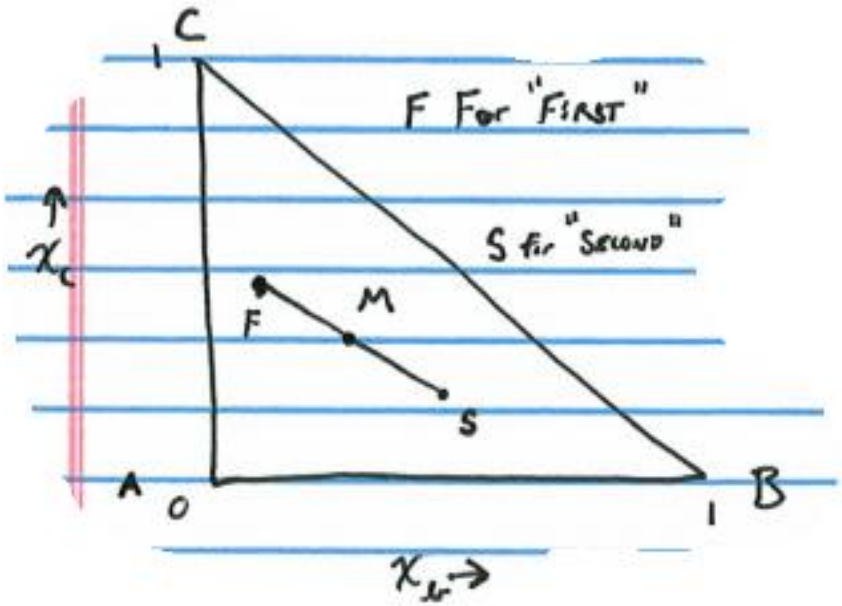
Equilateral Ternary Phase Diagrams

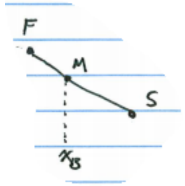
- Ternary Paper
- Be very cautious with this
- You need to read each component along lines parallel to that component's Zero axis
- We won't be using these very often (if at all…)

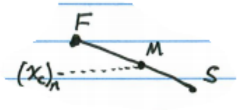


Liquid Liquid Extraction – Phase Diagrams

- Mass balance for a mixing step
- F is the first solution, S is the second solution
- F kg of mixture with composition $[(x_B)_F, (x_C)_F]$
- S kg of mixture with composition $[(y_B)_S, (y_C)_S]$
- M is for Mixture (of F and S)
- Total Mass M = F + S
- $\boxed{B}$ $$(\boldsymbol{x_B})_M = \frac{F(x_B)_F + S(y_B)_S}{F+S} = \frac{\text{mass of } B}{\text{Total mass}}$$
- $\boxed{C}$ $$(\boldsymbol{x_C})_M = \frac{F(x_C)_F + S(y_C)_S}{F+S} = \frac{\text{mass of } C}{\text{Total mass}}$$
- M will **<u>ALWAYS</u>** lie on the straight line between F and S
- Can calculate either $(\boldsymbol{x_B})_M$ or $(\boldsymbol{x_C})_M$ and locate point M on the line $\overline{\boldsymbol{FS}}$
- The **Lever Rule** states that the distance $\overline{\boldsymbol{FM}}$ relative to distance $\overline{\boldsymbol{MS}}$ is related to the relative magnitude of F and S.
  - It is better to actually do mass balances than to measure distances on a graph

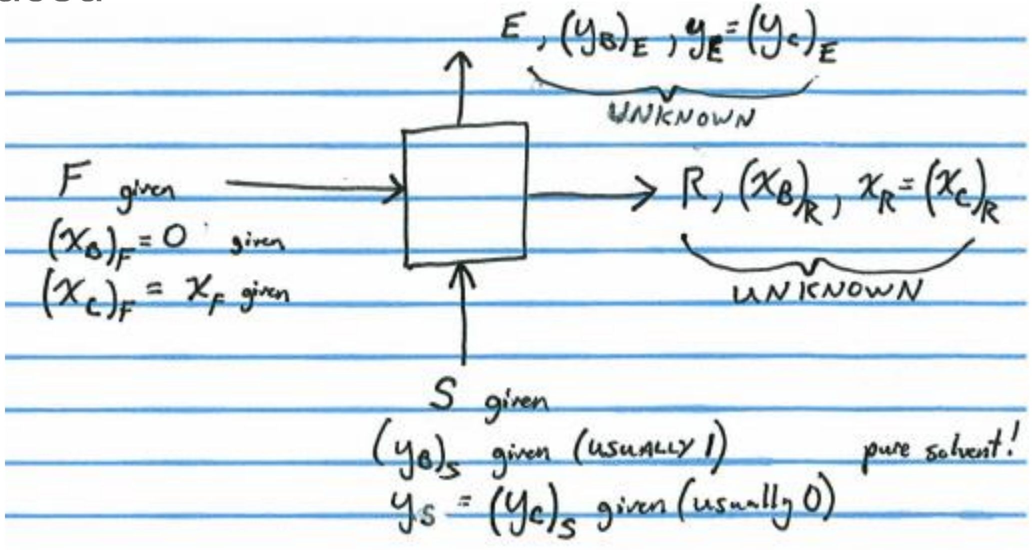


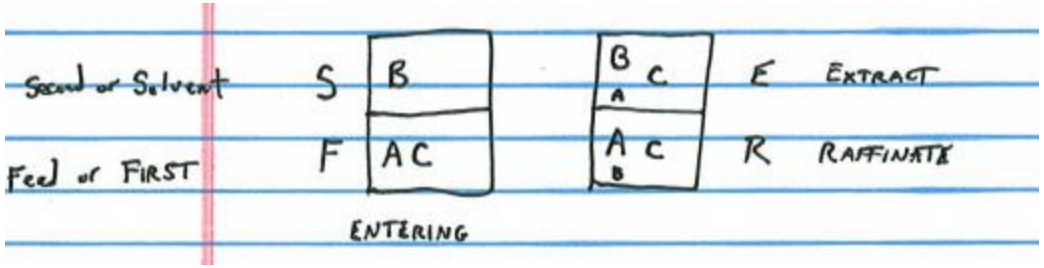




Single Stage LLE

- First stream composed of Diluent, A, and Solute, C is introduced to Second stream of Solvent
- Typically the First stream contains no solvent B, $(x_B)_F = 0$
- Typically the Second stream is Pure Solvent, $(y_B)_S = 1$
  - If the solvent is recycled this will not be the case
- E is for Extract and R is for Raffinate
- The relative size I have drawn the letters below is indicative of the relative amount in each phase

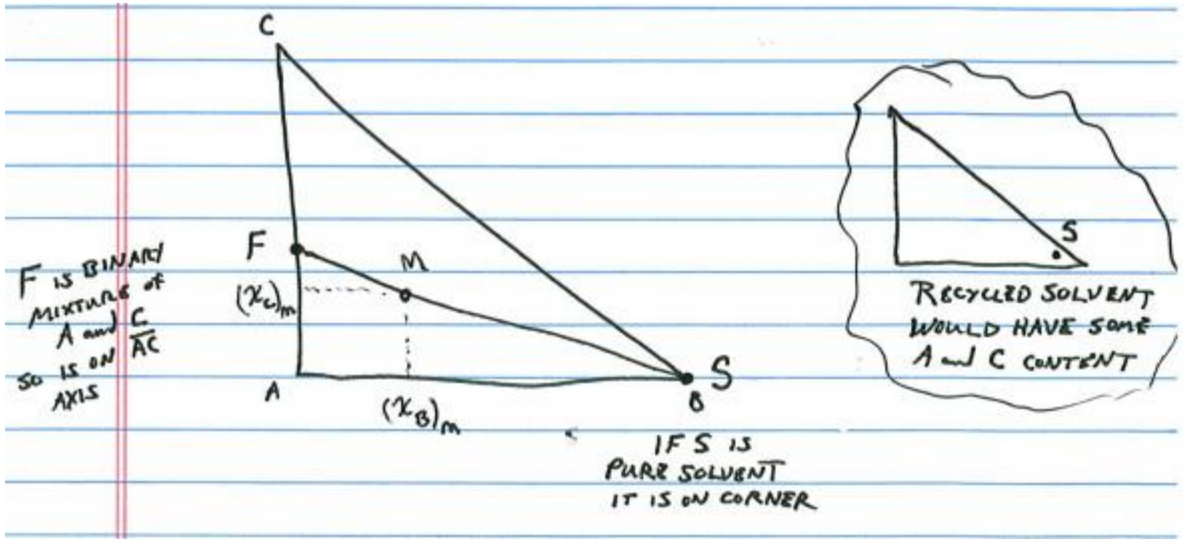




- Sometimes S can also be considered to refer to Solvent. Happily both second and solvent start with S!

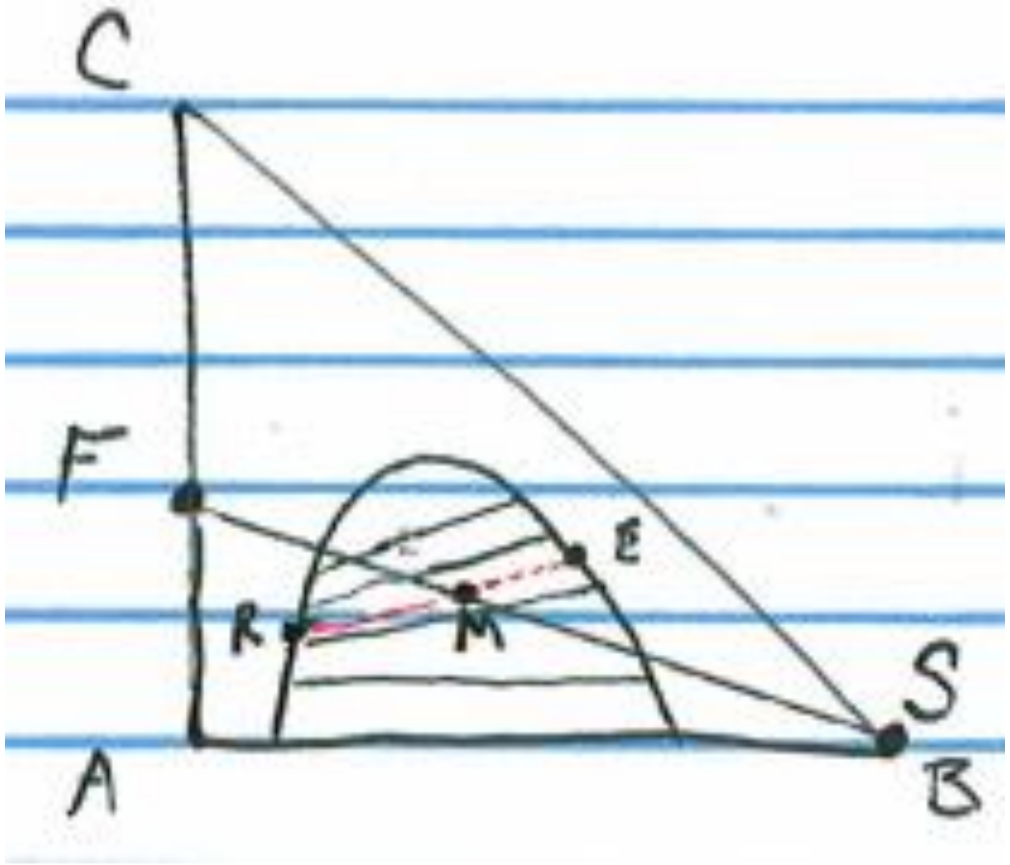
Single Stage Liquid Liquid Extraction

- Subscripts: F, S, E, R indicate to what STREAM we are referring
- Mass fraction of solute $(x_c)_\sim = x_\sim$; meaning that if we don't have a subscript indicating which component we are talking about, we are talking about the solute
- Mass fractions in the F and R phase are denoted by x
- Mass fractions in the S and E phase are denoted by y
- F lies on the $\overline{AC}$ axis
- If S is pure solvent it lies on the lower right corner, recycled solvent will not be on the corner
- M will lie on line $\overline{FS}$
- $x_M = \dfrac{Fx_F + Sy_S}{F+S}$
  - (subscript C has been dropped)



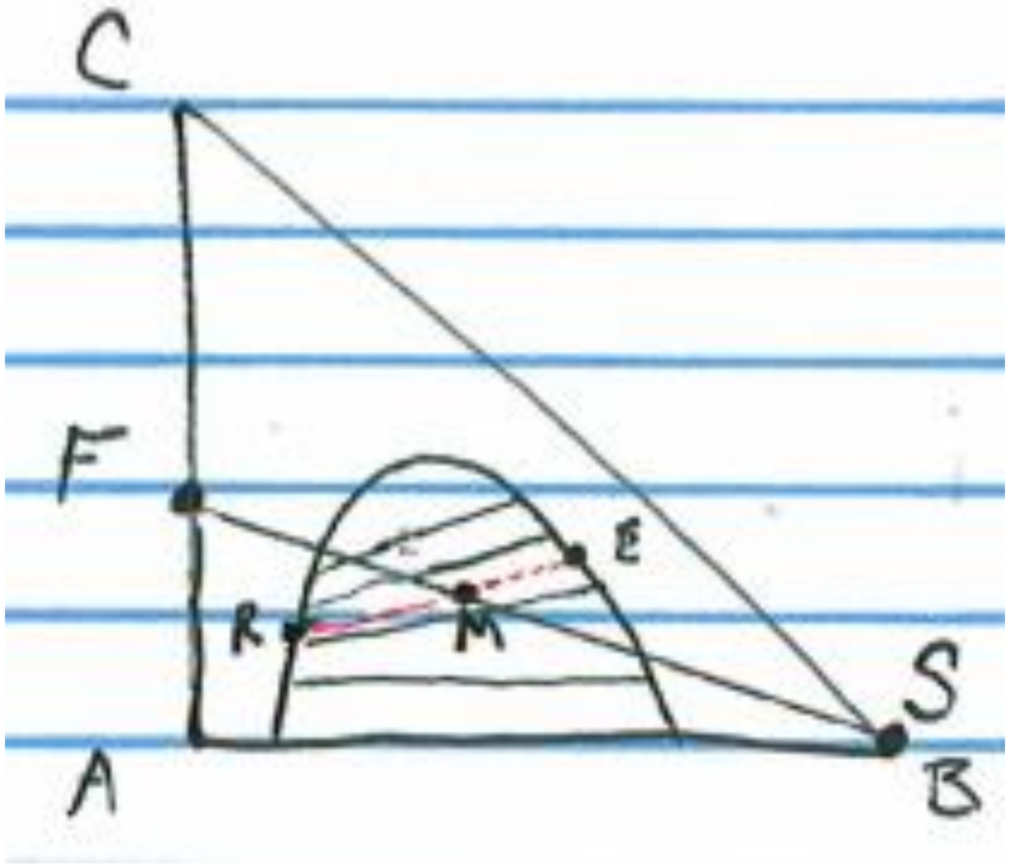
Single Stage Liquid Liquid Extraction

- Now that we have completed mass balances to locate M, let's add phase equilibria data (Tie Lines) to the graph
- Does M lie in the two phase region?
  - If yes, we will be able to extract material
  - If no, then we just has a bigger mess to clean up!
- M will most likely not fall on an existing tie line
- You may have to draw in an interpolated tie line (show in red on this diagram)



Single Stage Liquid Liquid Extraction

- The two points on the ends of M's tie line locate the position of R (Raffinate/A rich) and E (Extract/B rich) phases
- Now we have $(x_B)_R$ and x_R for the Raffinate
  and $(y_B)_E$ and y_E for the Extract
- We want to determine the total mass of both the Raffinate stage and the total mass of the extract stage
- Start with a mass balance of B
- $R(x_B)_R + E(y_B)_E = (R+E)(x_B)_M$
  - Note: M = R+E = F+S
- Rearrange algebraically
  - $E[(y_B)_E - (x_B)_M] = R[(x_B)_M - (x_B)_R]$



Single Stage Liquid Liquid Extraction

- After further mathematical manipulation

$$\frac{E}{R}=\frac{(x_B)_M-(x_B)_R}{(y_B)_E-(x_B)_M}$$

- or could perform a solute balance and in a similar fashion obtain

$$\frac{E}{R}=\frac{(x_C)_M-(x_C)_R}{(y_C)_E-(x_C)_M}=\frac{x_M-x_R}{y_E-x_M}$$

- Note that:

$$R+E=R\left(1+\frac{E}{R}\right)=M \text{ and } \qquad E=M-R$$

- Therefore

$$R=\frac{M}{1+{E}/{R}}$$

- The E/R equations on this page are the analytical expressions of the lever rule

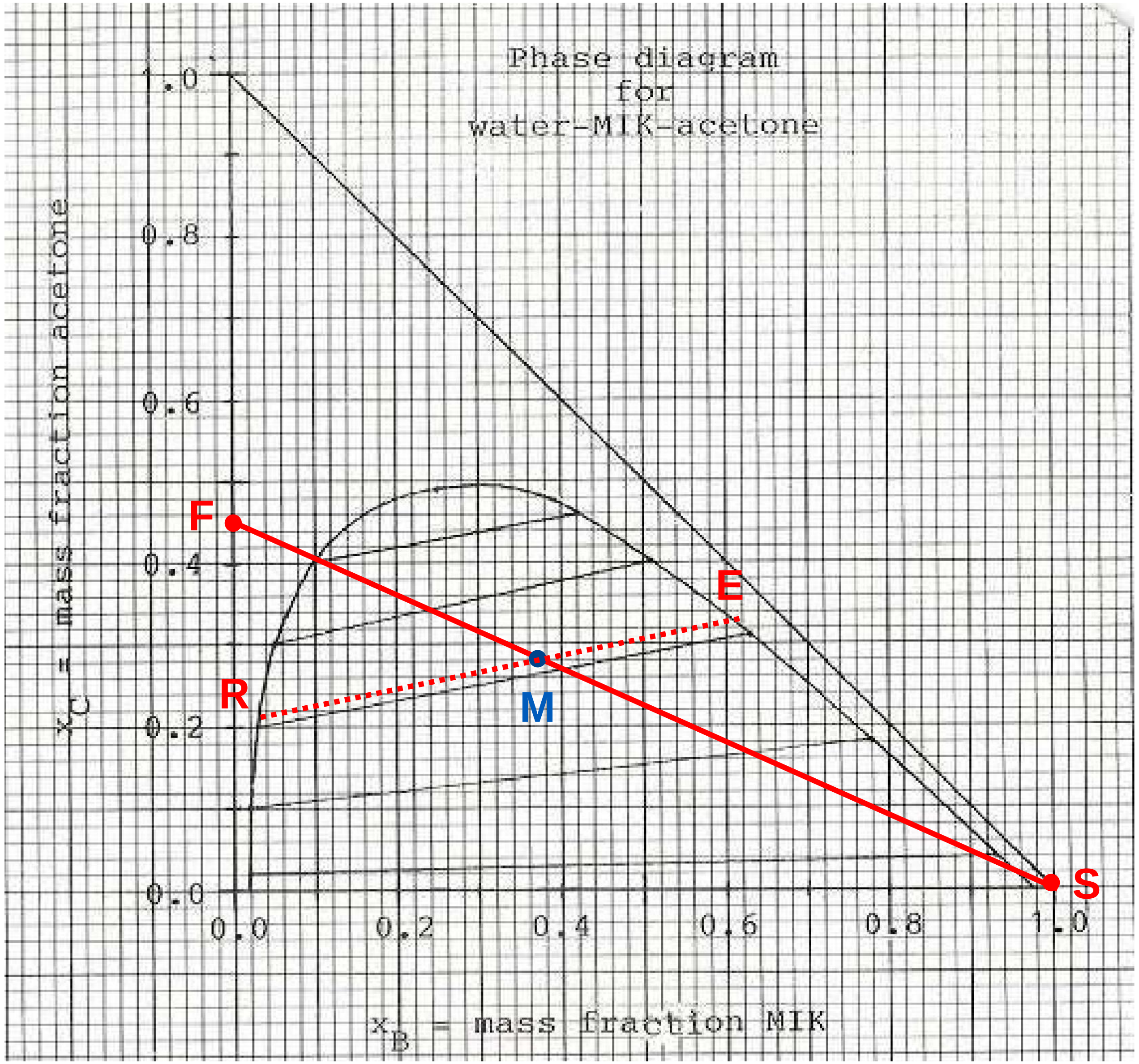
3. 100 kg of a binary mixture (45 mass percent acetone, 55 mass percent water) is mixed with pure MIK.

(a) If the amount of MIK used is 60 kg, the resulting ternary mixture will split into two phases. What are the masses and compositions of the raffinate and extract phases formed?

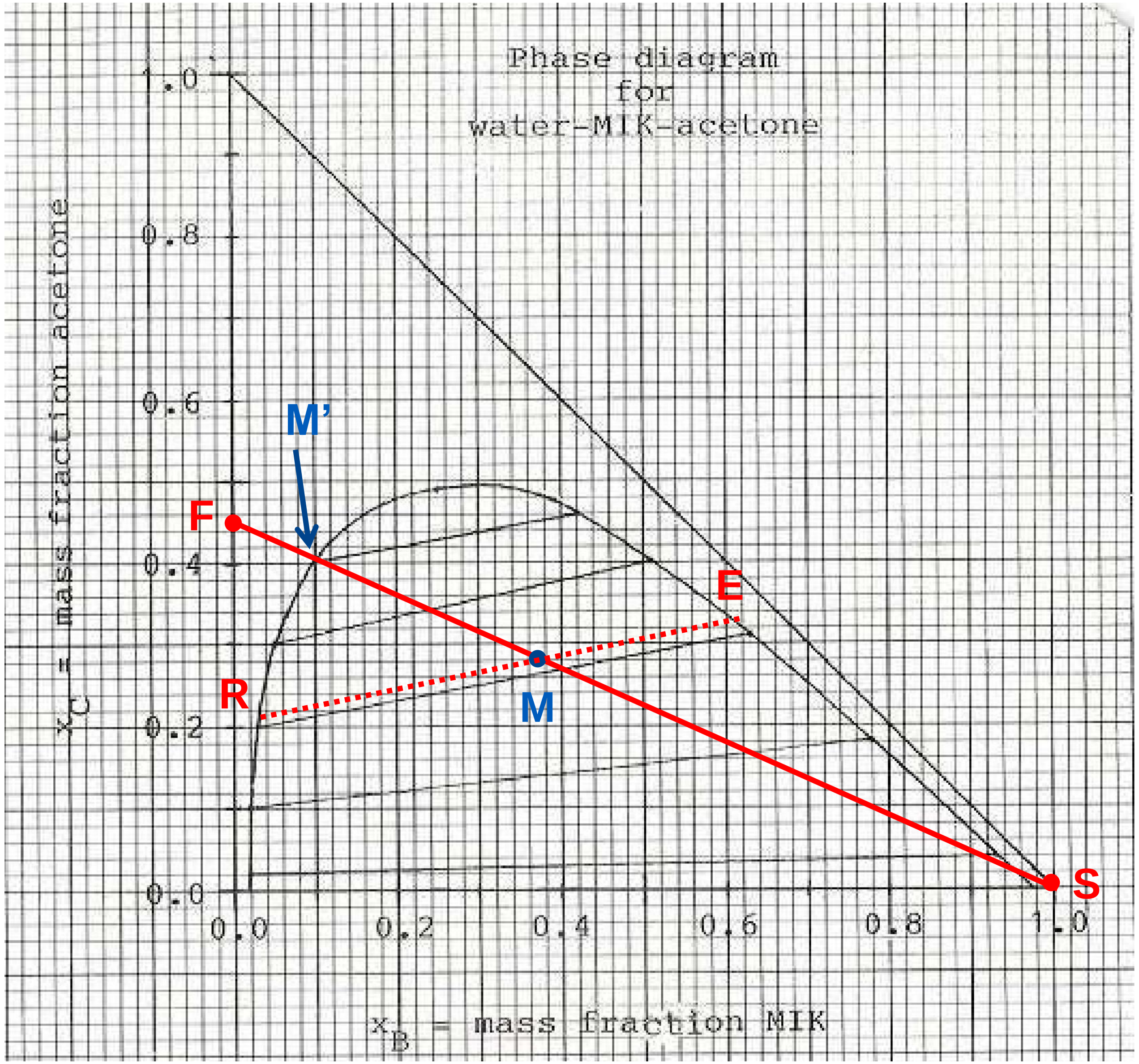
(b) What is the minimum amount of MIK required to produce a mixture that separates into two phases.

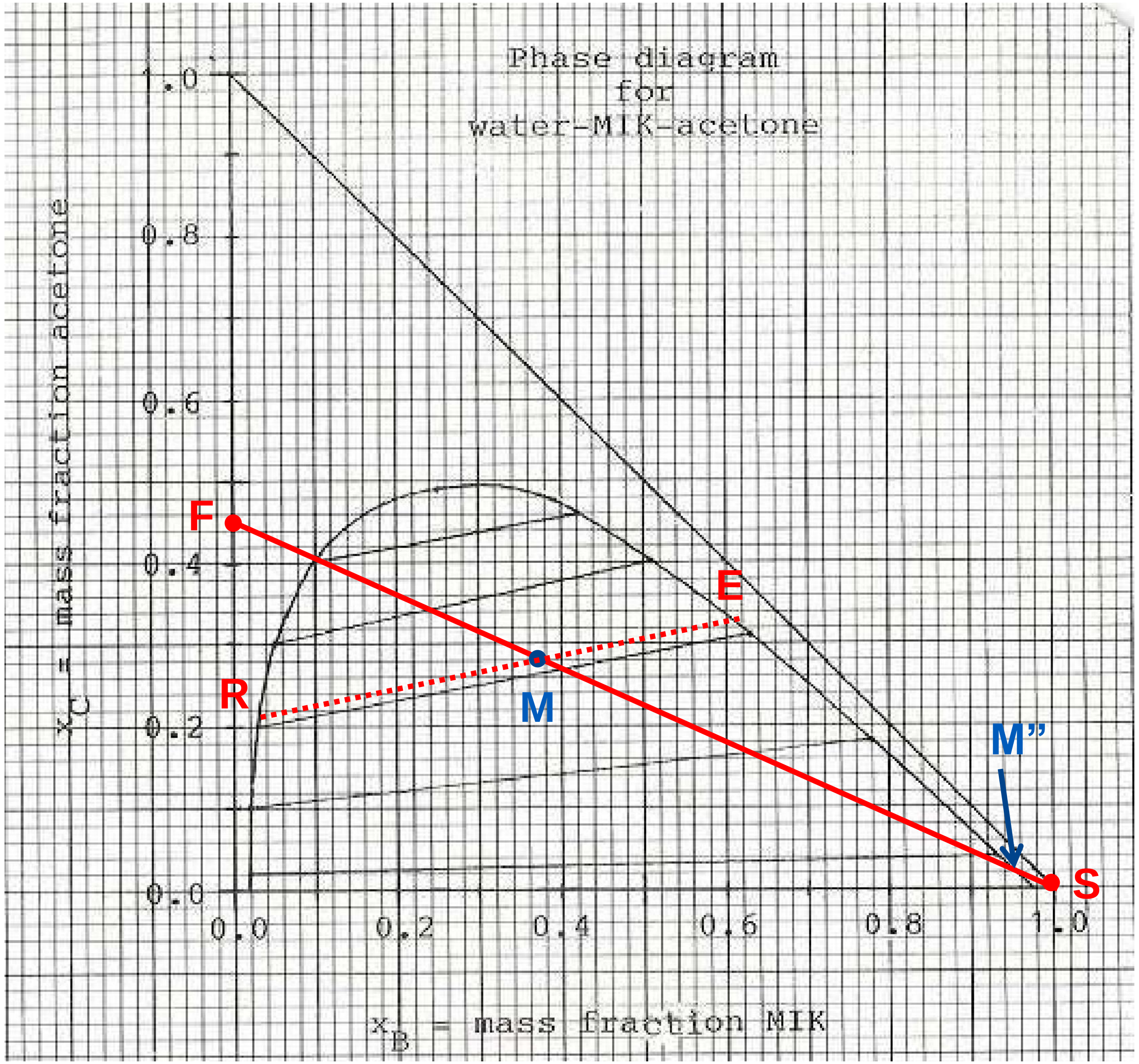
(c) What is the maximum amount of MIK that can be added such that the resulting mixture still splits into two phases?

Phase diagram is given on separate sheet. Parts (b) and (c) will require a little thought, but you can handle it.



$$\frac{E}{R} = \frac{(x_C)_M - (x_C)_R}{(y_C)_E - (x_C)_M} = \frac{x_M - x_R}{y_E - x_M}$$


Phase diagram
for
water-MIK-acetone
1.0
0.8
0.6
0.4
0.2
0.0
x_C = mass fraction acetone
0.0
0.2
0.4
0.6
0.8
1.0
x_B = mass fraction MIK
M'
F
E
R
M
S


Phase diagram
for
water-MIK-acetone
x_C = mass fraction acetone
x_B = mass fraction MIK
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
F
E
R
M
M"
S