

CE407 SEPARATIONS

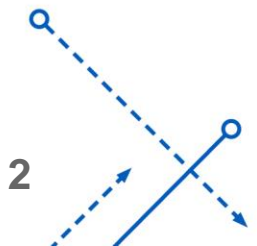
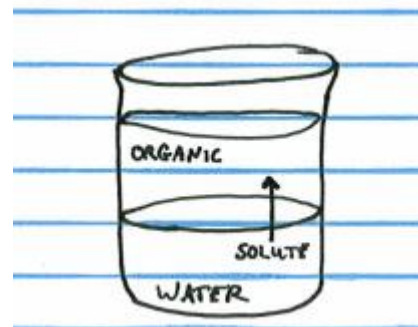
Lecture 14

Instructor: David Courtemanche



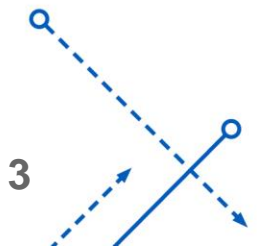
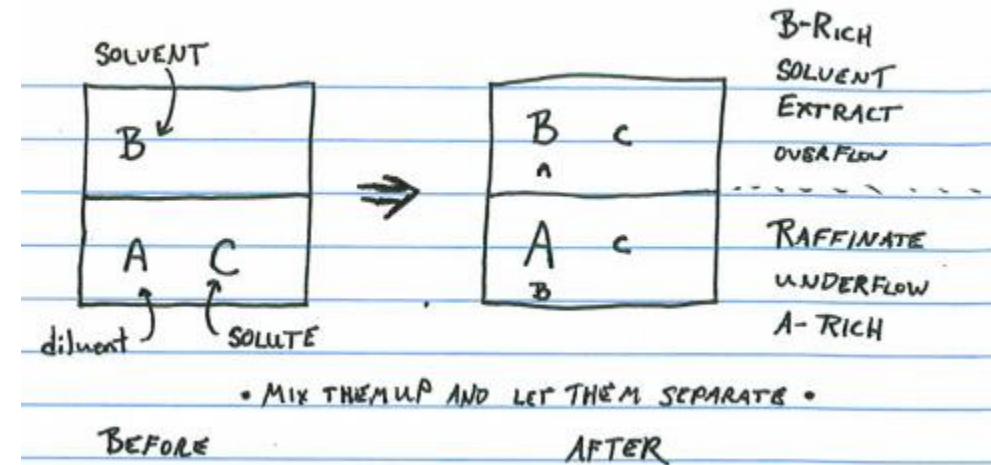
Liquid Liquid Extraction McSH pp772-791 Treybal pp 433-453

- 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...



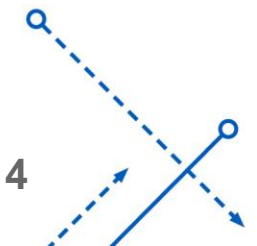
Liquid Liquid Extraction

- 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



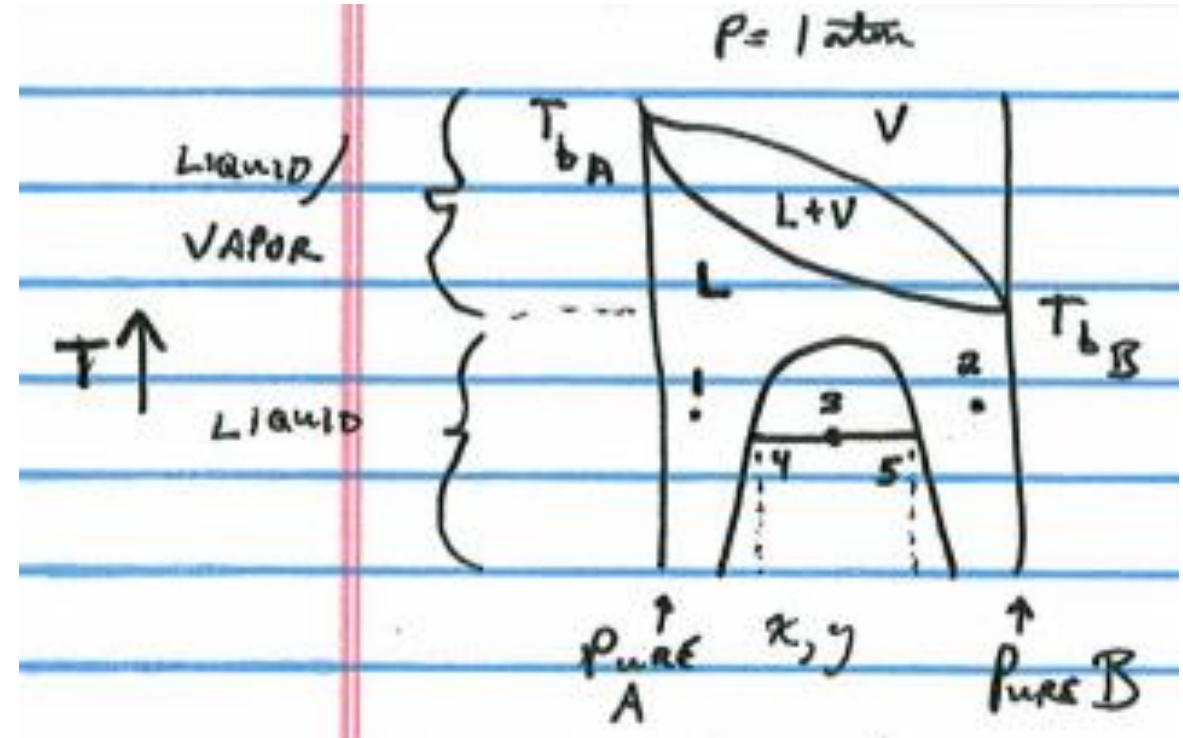
Liquid Liquid Extraction

- 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

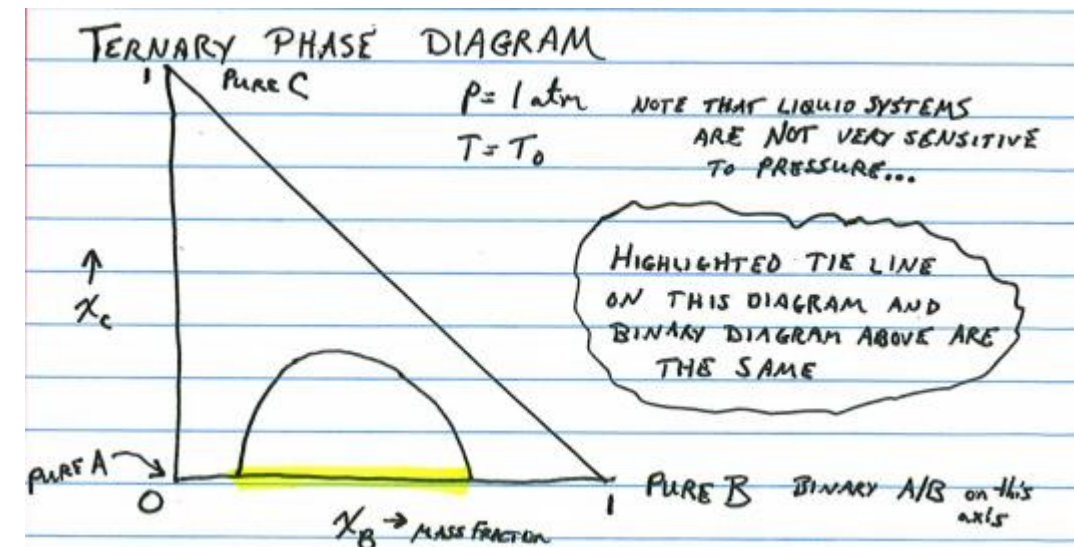


Note:

- 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

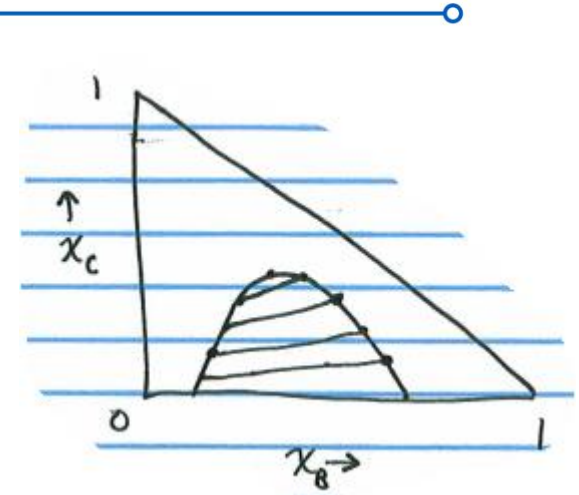
Liquid Liquid Extraction – Phase Diagrams

- 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 x_B and x_C as axes
 - Because $x_A = 1 - x_B - x_C$ 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

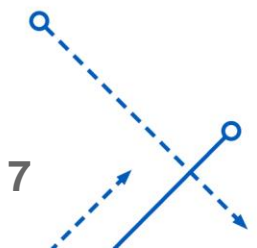


Liquid Liquid Extraction – Phase Diagrams

- 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

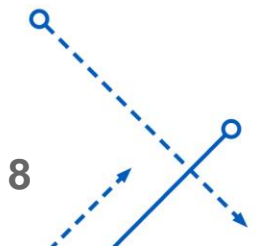
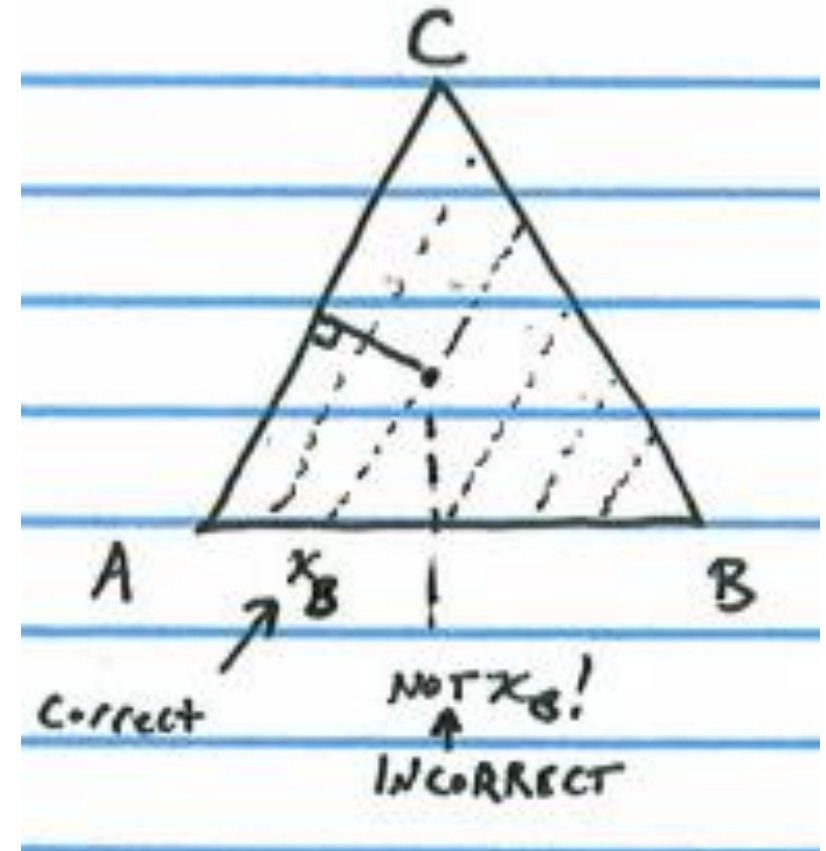


| Raffinate | | Extract | |
|-----------|-------|---------|-------|
| x_B | x_C | x_B | x_C |
| ~ | ~ | ~ | ~ |
| ~ | ~ | ~ | ~ |



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

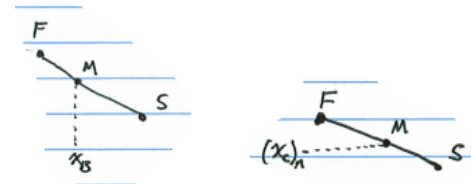
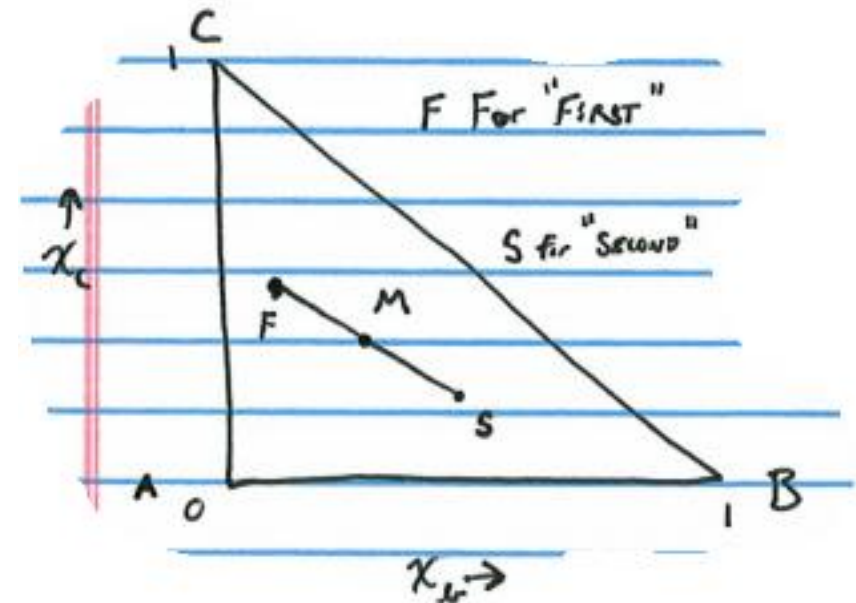
- Mass balance for a mixing step
- F is the first solution, S is the second solution
- F kg of mixture with composition $[(x_B)_F, (x_C)_F]$
- S kg of mixture with composition $[(y_B)_S, (y_C)_S]$
- M is for Mixture (of F and S)
- Total Mass $M = F + S$

• B $(x_B)_M = \frac{F(x_B)_F + S(y_B)_S}{F+S} = \frac{\text{mass of B}}{\text{Total mass}}$

• C $(x_C)_M = \frac{F(x_C)_F + S(y_C)_S}{F+S} = \frac{\text{mass of C}}{\text{Total mass}}$

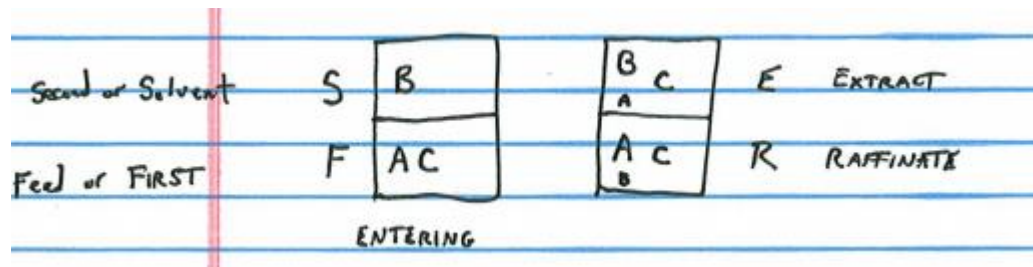
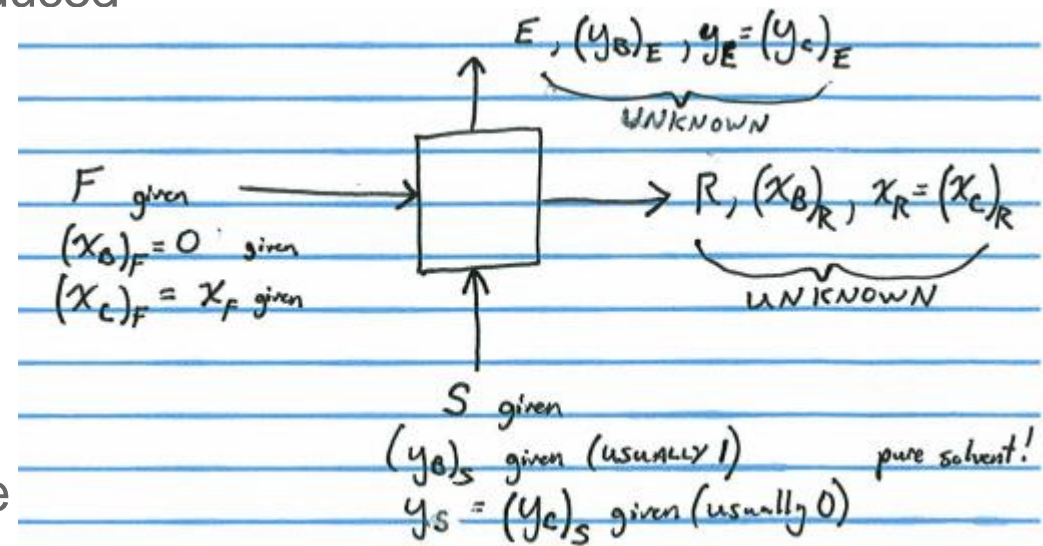
- M will **ALWAYS** lie on the straight line between F and S
- Can calculate either $(x_B)_M$ or $(x_C)_M$ and locate point M on the line \overline{FS}
- The **Lever Rule** states that the distance \overline{FM} relative to distance \overline{MS} is related to the relative magnitude of F and S.

- It is better to actually do mass balances than to measure distances on a graph



Single Stage LLE

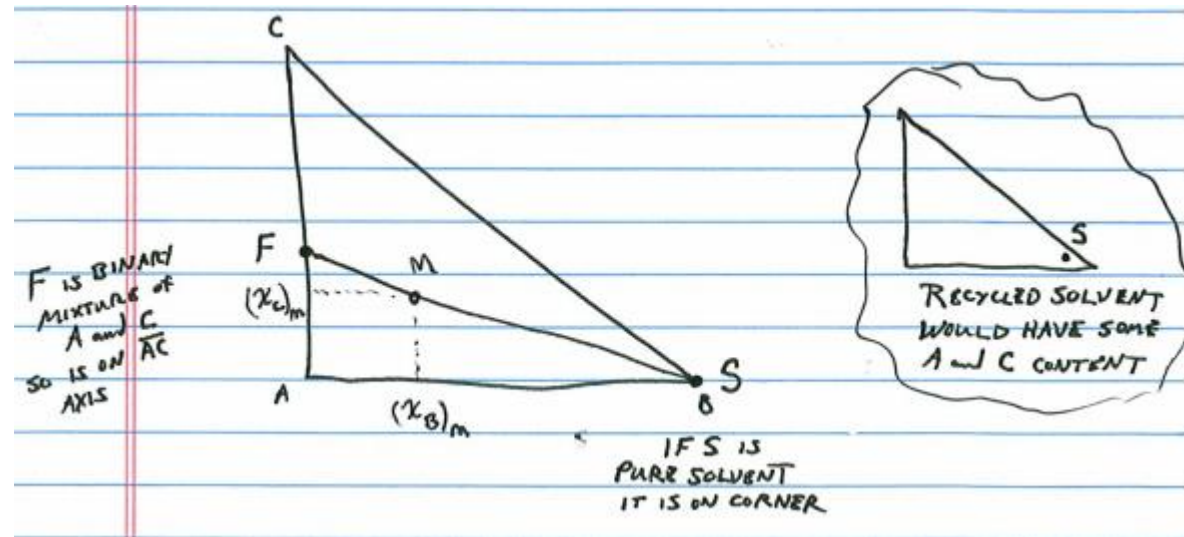
- First stream composed of Diluent, A, and Solute, C is introduced to Second stream of Solvent
- Typically the First stream contains no solvent B, $(x_B)_F = 0$
- Typically the Second stream is Pure Solvent, $(x_B)_S = 1$
 - If the solvent is recycled this will not be the case
- E is for Extract and 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!

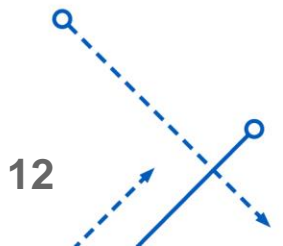
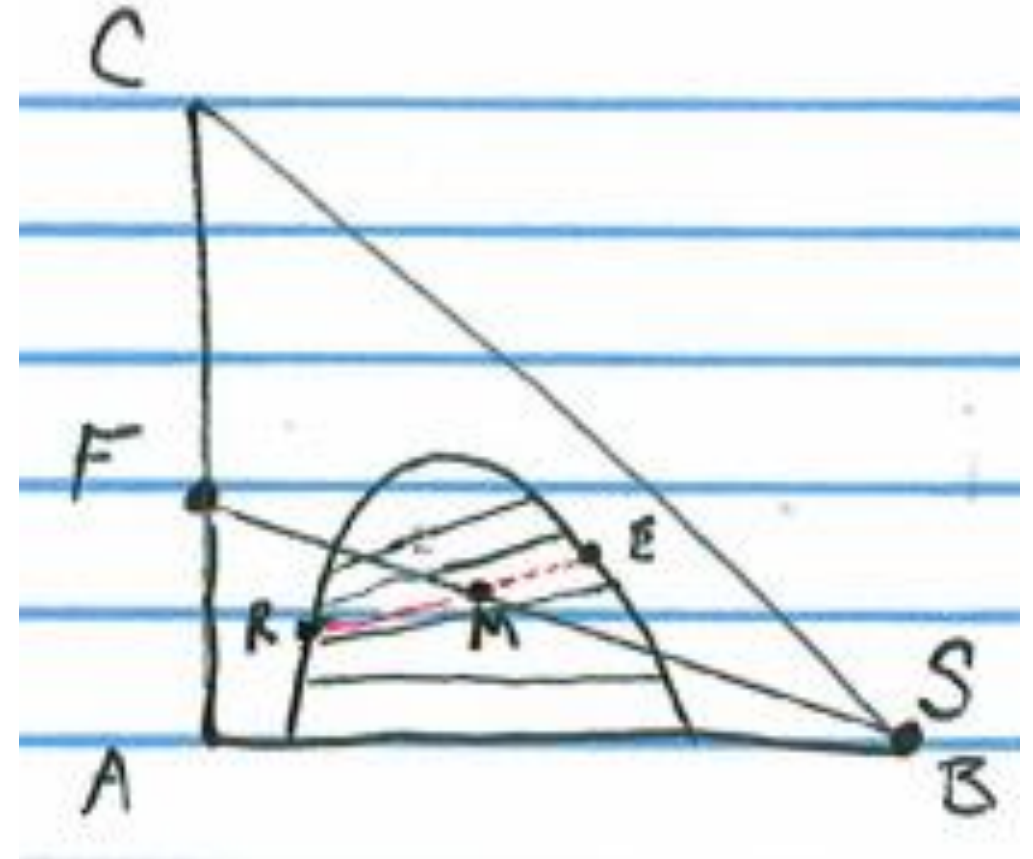
Single Stage Liquid Liquid Extraction

- 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}
- $$x_M = \frac{Fx_F + Sy_S}{F+S}$$
 - (subscript C has been dropped)



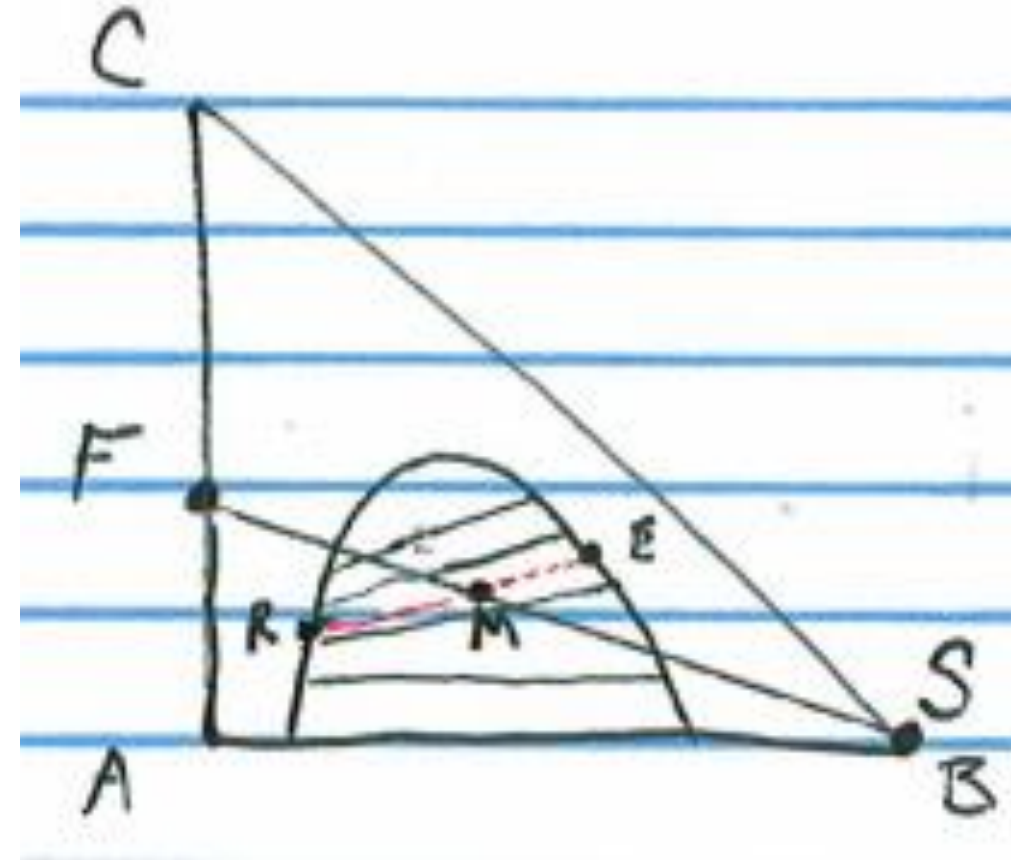
Single Stage Liquid Liquid Extraction

- 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:

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

- Therefore

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

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