Lecture 7

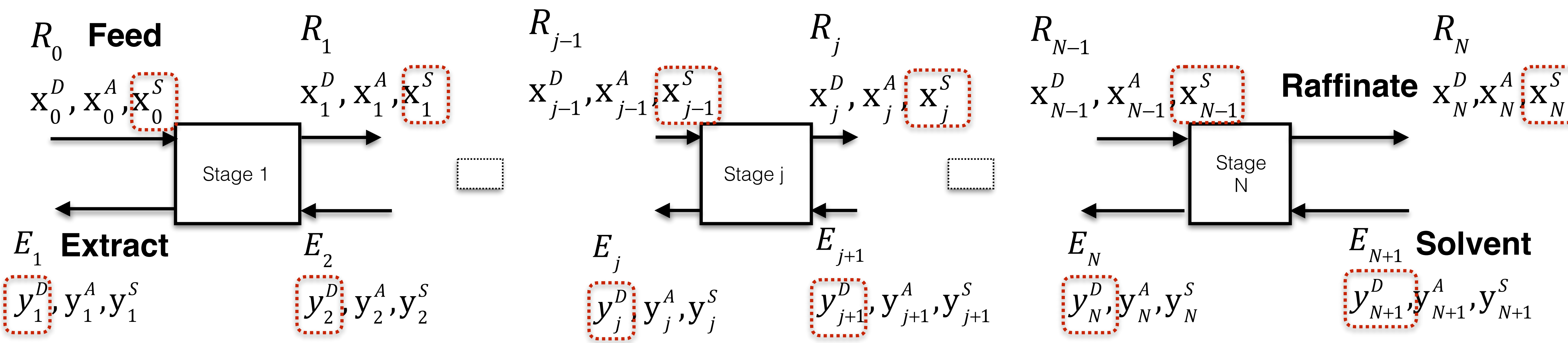
Liquid-Liquid Extraction

(partially miscible solvent and diluent)

Intended learning outcome

1. Analyze the difference in system when solvent and diluent are partially miscible.
2. Analyze triangular phase diagram for reading composition of mixture.
3. Analyze single-stage extraction using triangular diagram.
4. Calculate number of stages for countercurrent operation using triangular diagram.

Partially miscible solvent/diluent



Nomenclature

D: Diluent

A: Solute

S: Solvent

R = Raffinate

E = Extract

x_0^D = mole fraction of diluent in Raffinate stream entering stage 1

x_0^S = mole fraction of solvent in Raffinate stream entering stage 1

x_0^A = mole fraction of solute in Raffinate stream entering stage 1

$$R_0 \neq R_1 \neq \ldots R_{j-1} \neq R_j \neq \ldots R_{N-1} \neq R_N$$

$$E_1 \neq E_2 \neq \ldots E_j \neq E_{j+1} \neq \ldots E_N \neq E_{N+1}$$

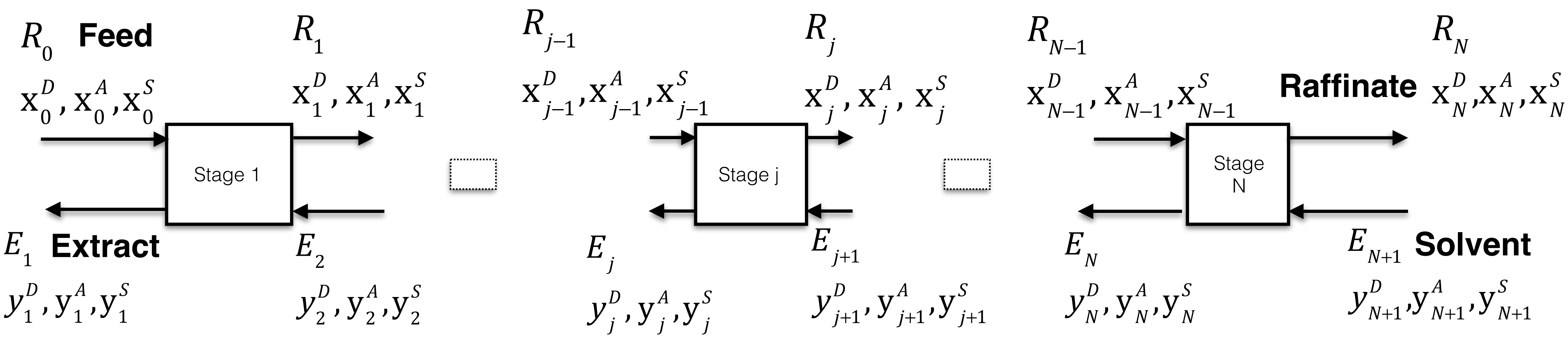
Diluent flow rate is not constant

$$F_{D,0} \neq F_{D,1} \neq F_{D,1} \ldots\ldots \neq F_{D,N+1}$$

Solvent flow rate is not constant

$$F_{S,0} \neq F_{S,1} \neq F_{S,1} \ldots\ldots \neq F_{S,N+1}$$

Partially miscible solvent/diluent



$$x_j^D + x_j^A + x_j^S = 1$$

$$y_j^D + y_j^A + y_j^S = 1$$

At stage j

1. x_j^D, x_j^A, x_j^S and y_j^D, y_j^A, y_j^S are in equilibrium (streams leaving the stage).
2. x_j^D, x_j^A, x_j^S and $y_{j+1}^D, y_{j+1}^A, y_{j+1}^S$ are part of the operating line (streams connecting two stages).

EPFL

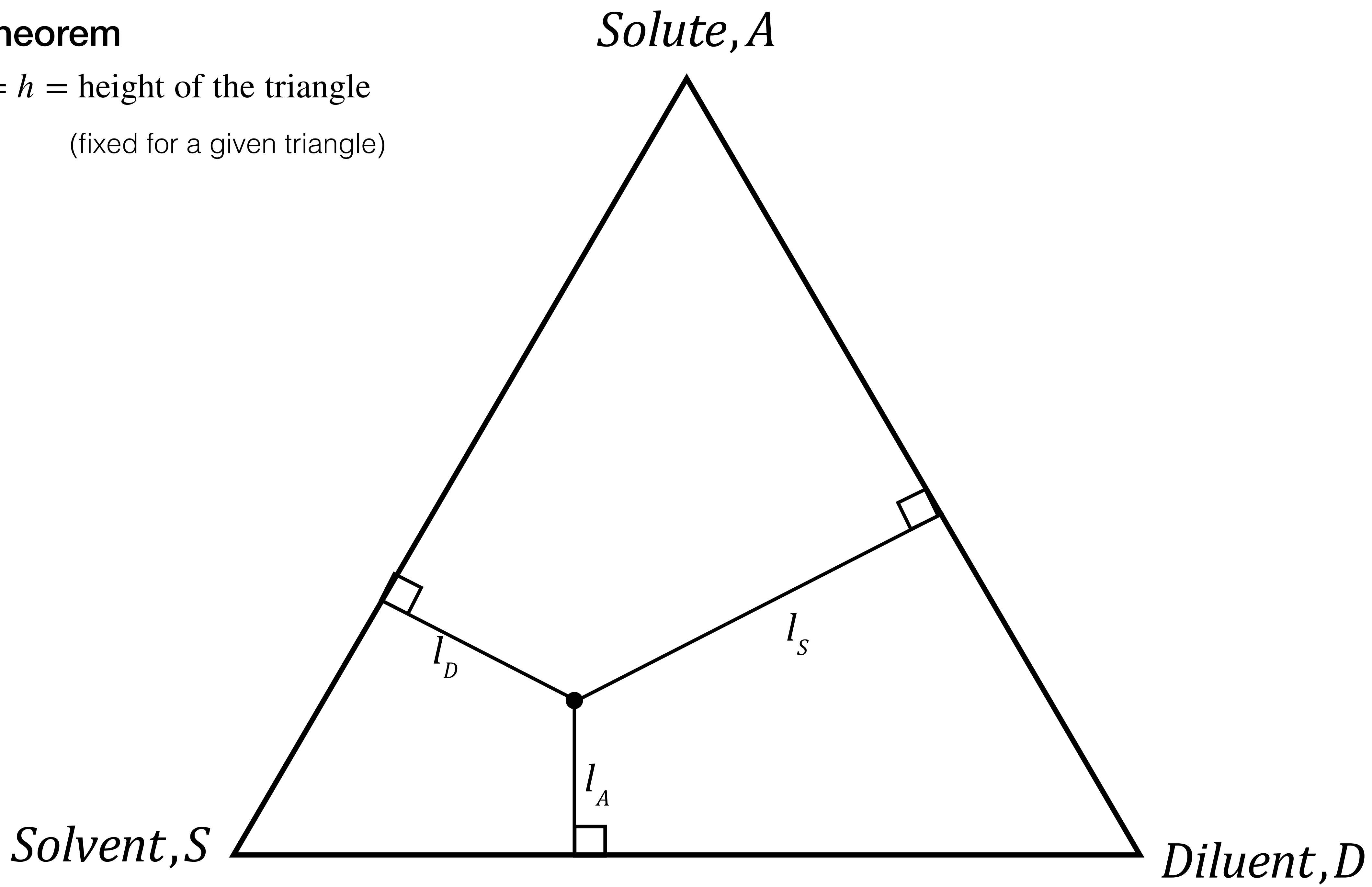
Equilibrium relationship:
Reading composition from triangular phase diagrams

Equilateral triangle

Viviani's theorem

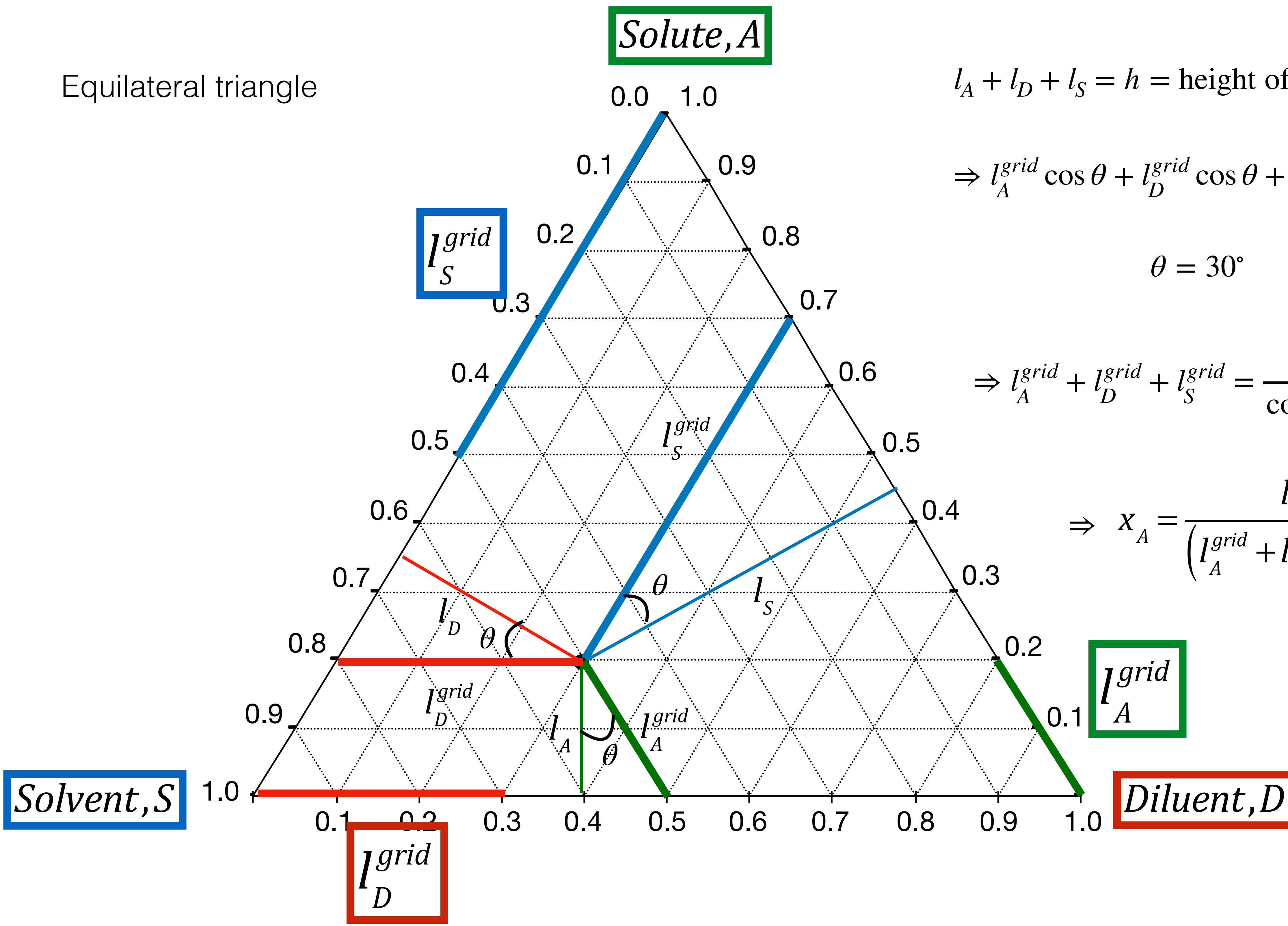
$l_A + l_D + l_S = h =$ height of the triangle

(fixed for a given triangle)



Reading composition from triangular diagrams

Equilateral triangle



$$l_A + l_D + l_S = h = \text{height of the triangle}$$

$$\Rightarrow l_A^{grid}\cos\theta + l_D^{grid}\cos\theta + l_S^{grid}\cos\theta = h$$

$$\theta = 30^\circ$$

$$\Rightarrow l_A^{grid} + l_D^{grid} + l_S^{grid} = \frac{h}{\cos 30} = \frac{2h}{\sqrt{3}} = a = 1$$

$$\Rightarrow x_A = \frac{l_A^{grid}}{\left(l_A^{grid} + l_D^{grid} + l_S^{grid}\right)} = l_A^{grid}$$

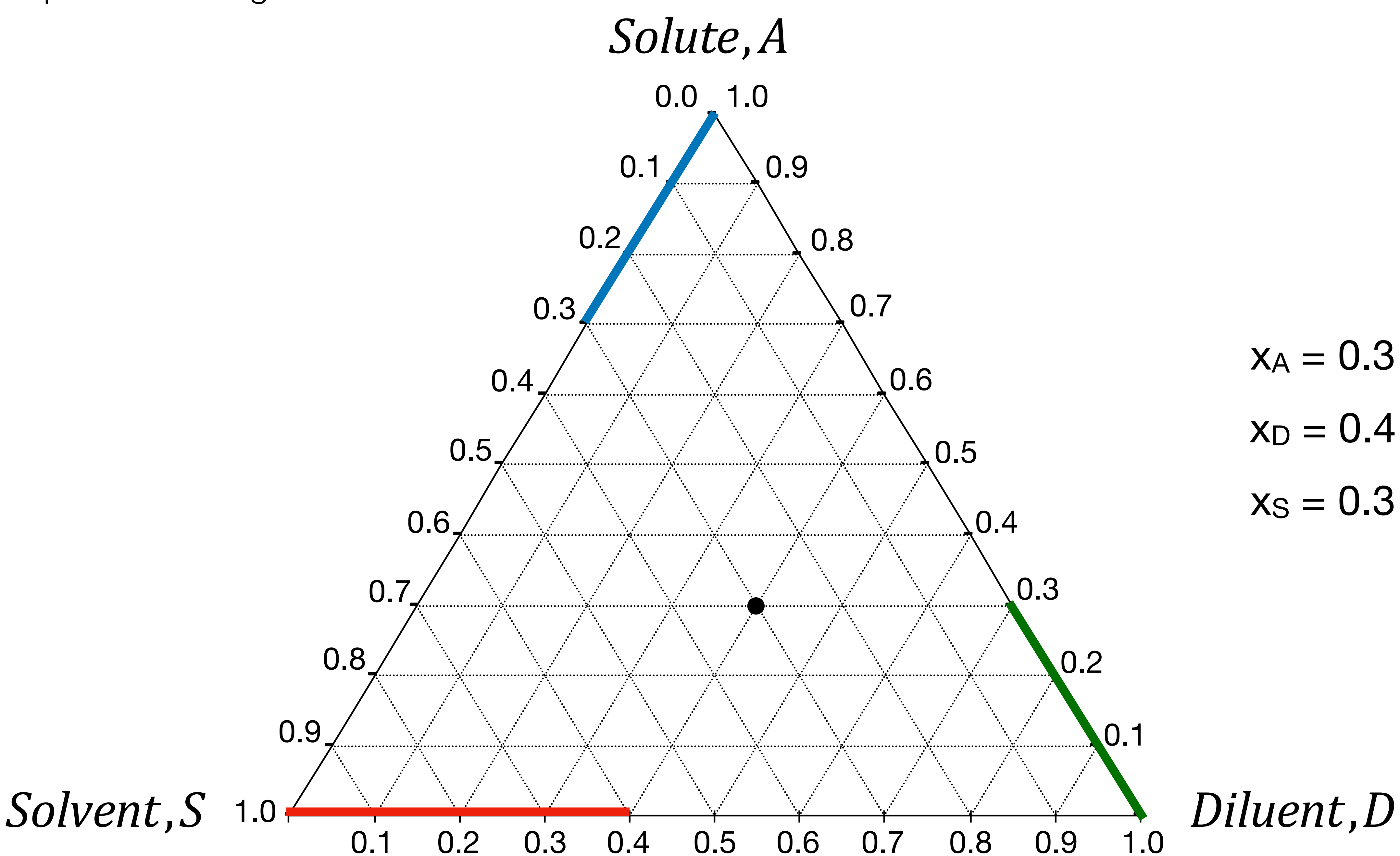
$$x_D = l_D^{grid}$$

$$x_S = l_S^{grid}$$

EPFL

Reading composition from triangular diagrams

Equilateral triangle



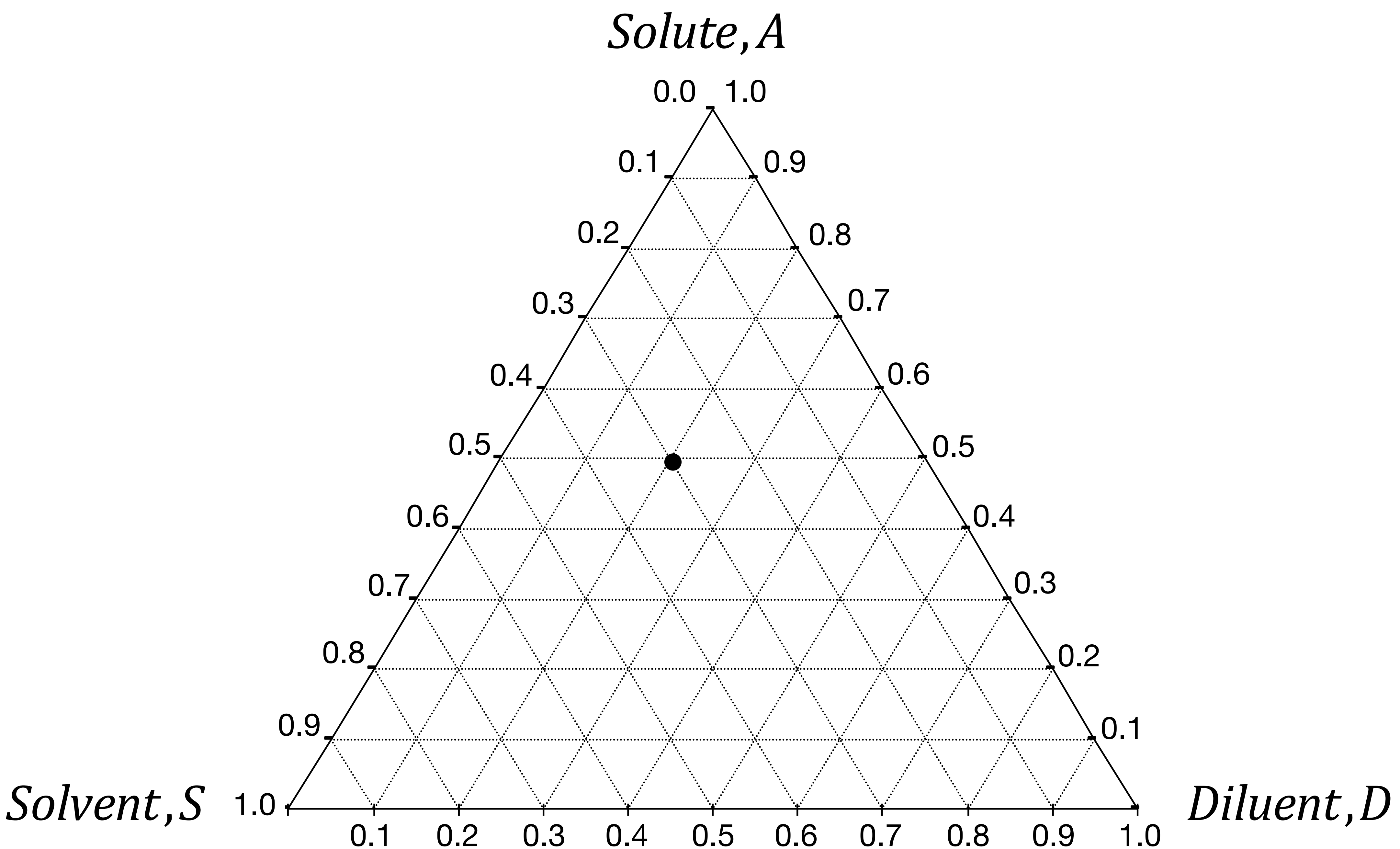
$x_A = 0.3$

$x_D = 0.4$

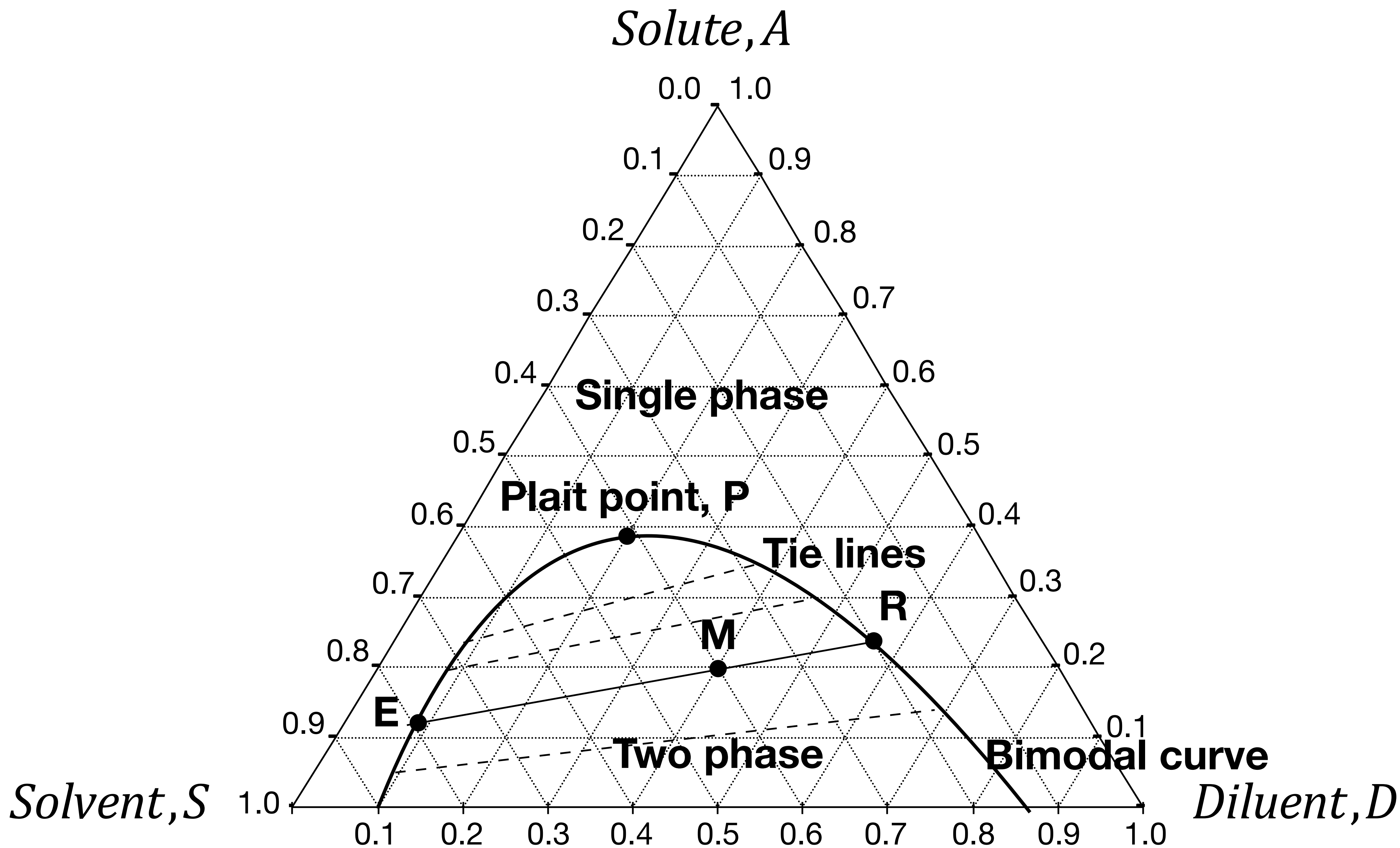
$x_S = 0.3$

What is the composition of solute and diluent?

A. 0.8 and 0.2
B. 0.3 and 0.5
C. 0.5 and 0.2
D. 0.5 and 0.8

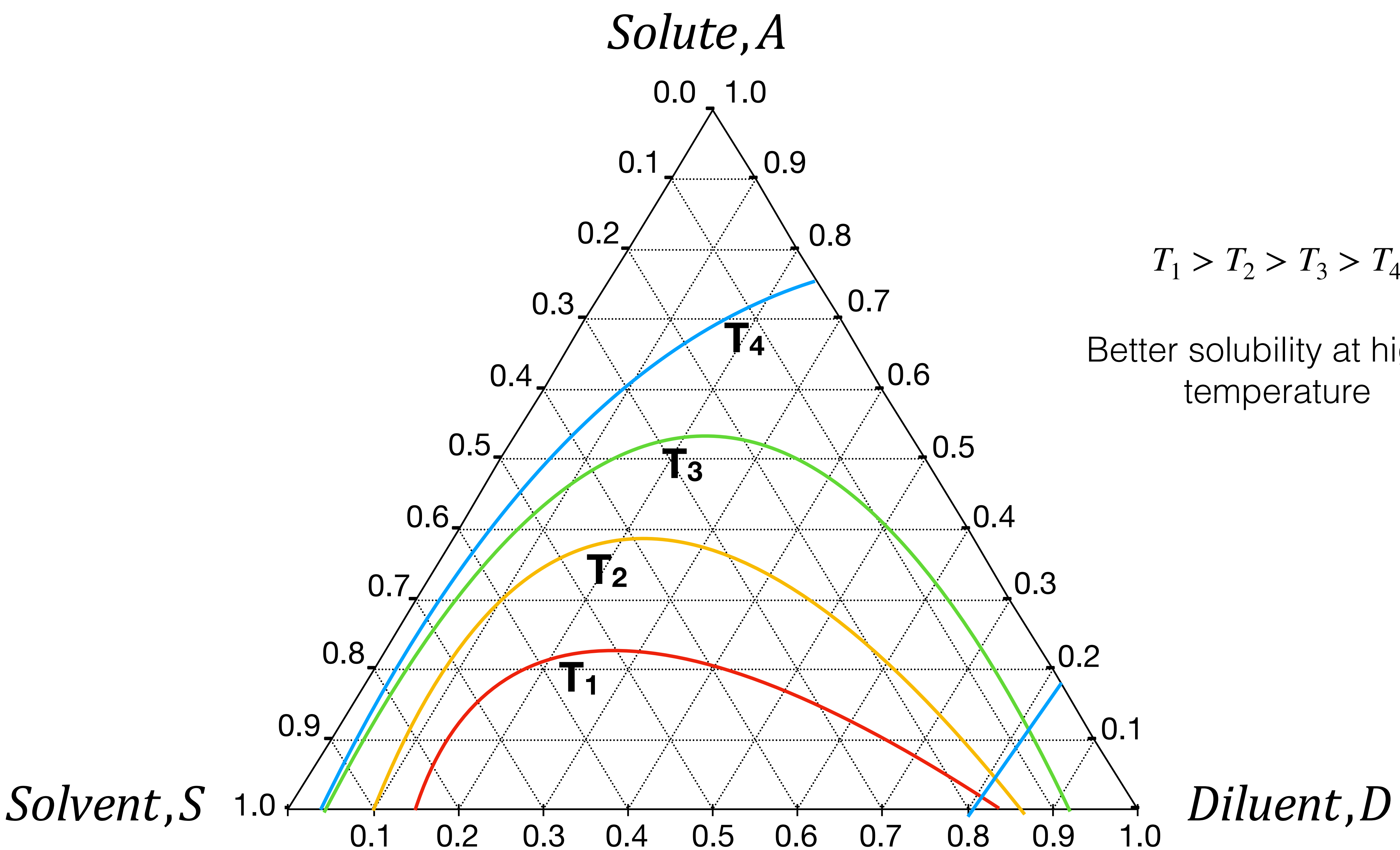


Equilibrium relationship in partially miscible solvent/diluent case



EPFL

Effect of temperature



$T_1 > T_2 > T_3 > T_4$

Better solubility at higher temperature

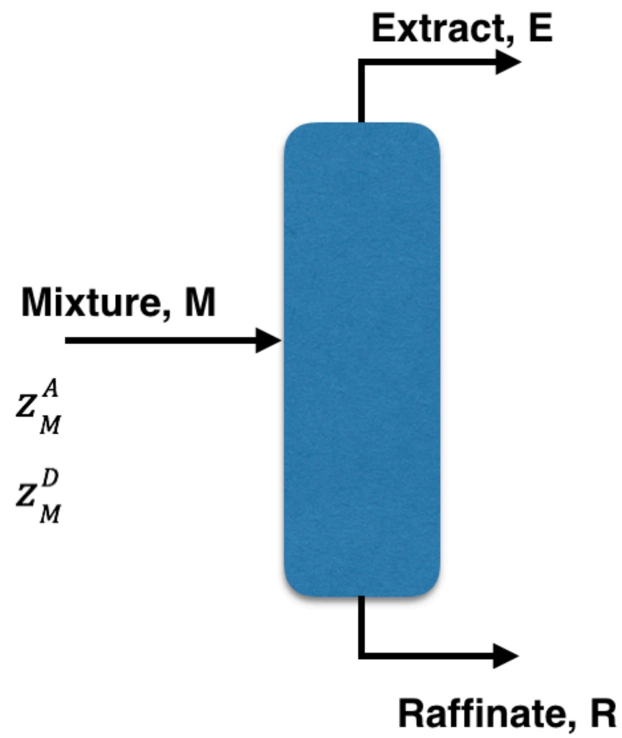
Calculations for partially miscible mixture

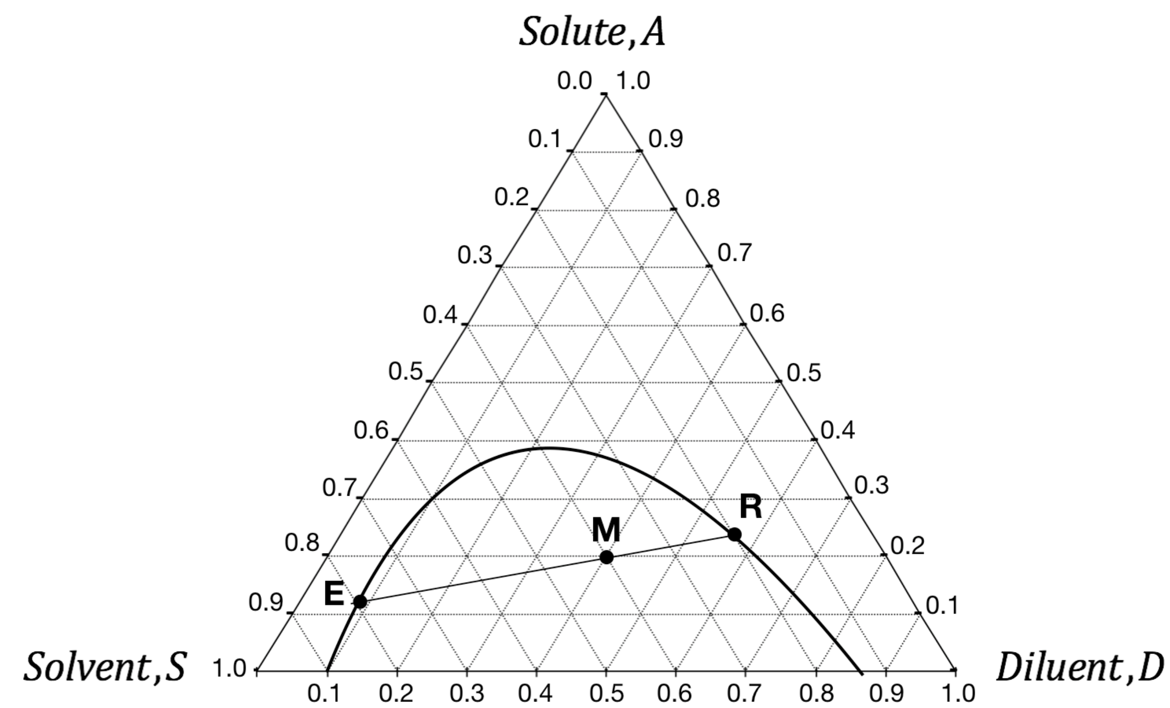
Consider two stream, E and R, which mix to form M

$$M = E + R$$

$$Mz_M^A = Ey_E^A + Rx_R^A$$

$$Mz_M^D = Ey_E^D + Rx_R^D$$





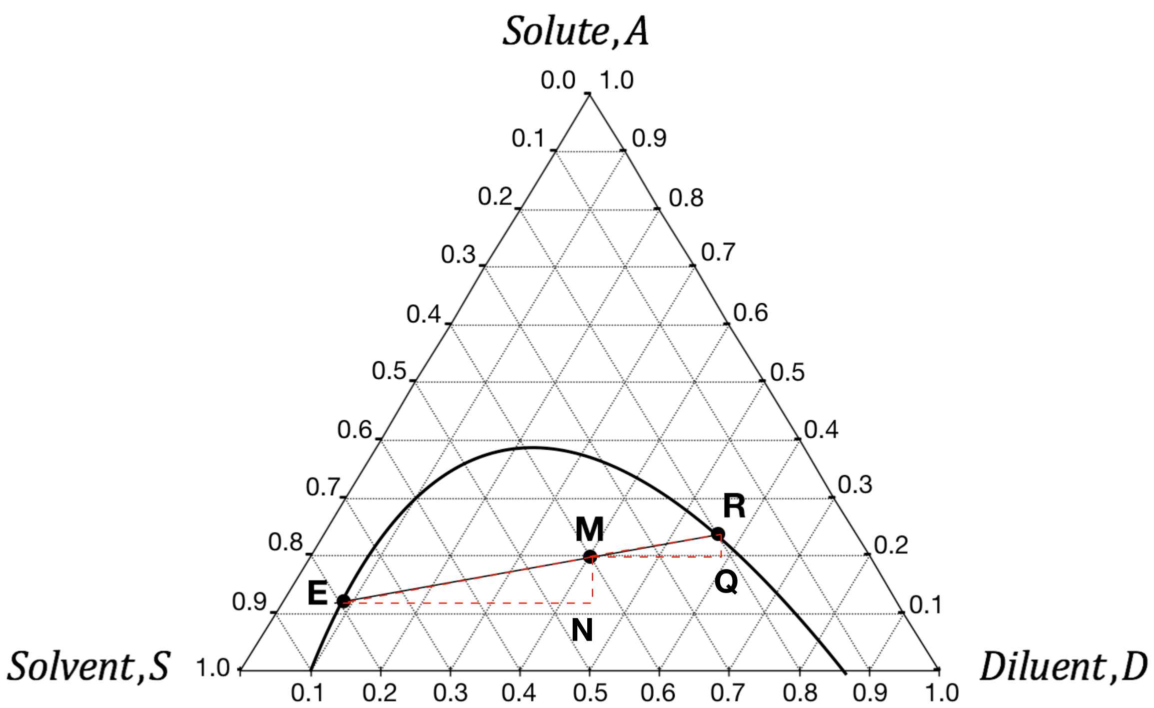
$$z_M^A = \frac{Ey_E^A + Rx_R^A}{M} = \frac{Ey_E^A + Rx_R^A}{E + R}$$

$$z_M^D = \frac{Ey_E^D + Rx_R^D}{M} = \frac{Ey_E^D + Rx_R^D}{E + R}$$

Can be used to calculate composition of M when the flow rates and the compositions of the E and R streams is known

Lever-arm rule

$$z_M^A = \frac{Ey_E^A + Rx_R^A}{E+R} \qquad = \frac{y_E^A + \left(\frac{R}{E}\right)x_R^A}{1+\left(\frac{R}{E}\right)}$$



$$z_M^A + z_M^A\left(\frac{R}{E}\right) = y_E^A + \left(\frac{R}{E}\right)x_R^A$$

$$\frac{R}{E} = \frac{y_E^A - z_M^A}{z_M^A - x_R^A} = \frac{\overline{NM}}{\overline{QR}} = \frac{\overline{EM}}{\overline{MR}}$$

The lever-arm rule

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

$$\frac{\overline{EM}}{\overline{MR}} + 1 = \frac{\overline{EM} + \overline{MR}}{\overline{MR}} = \frac{\overline{ER}}{\overline{MR}}$$

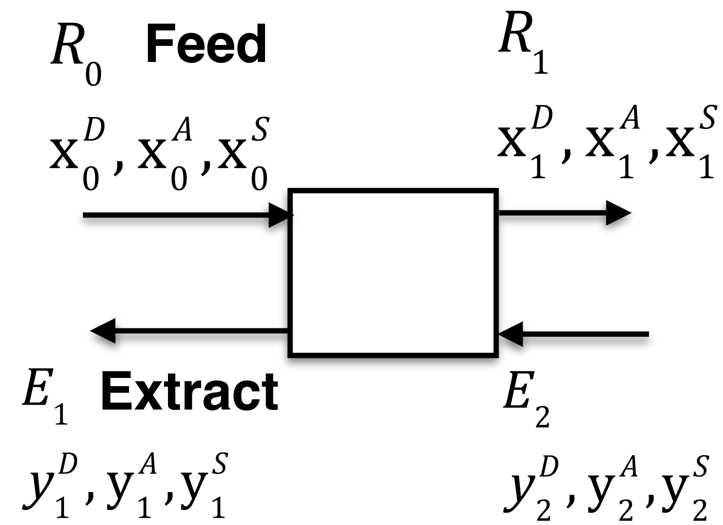
$$\frac{E}{M} = \frac{\overline{MR}}{\overline{ER}}$$

$$\frac{R}{M} = \frac{\overline{EM}}{\overline{ER}}$$

Single-stage extraction

Specified

R_0 | E_2
x_0^D, x_0^A, x_0^S | y_2^D, y_2^A, y_2^S



Need to calculate

R_1 | E_1
x_1^D, x_1^A, x_1^S | y_1^D, y_1^A, y_1^S

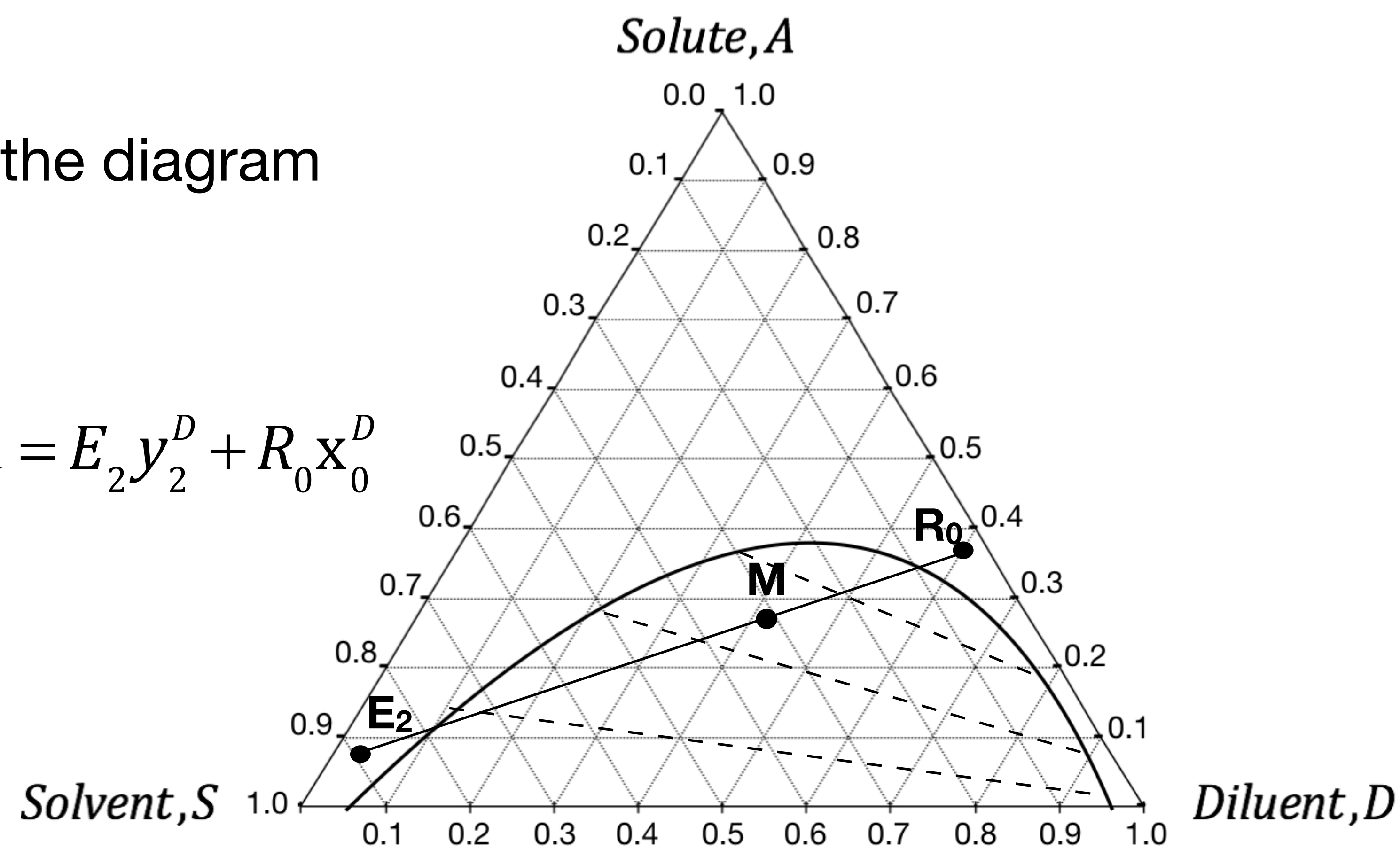
1. Start with identifying R_0 and E_2 on the diagram

2. Calculate specification of mixture

$$M = E_2 + R_0 \qquad Mz_M^A = E_2 y_2^A + R_0 x_0^A \qquad Mz_M^D = E_2 y_2^D + R_0 x_0^D$$

$$z_M^A = \frac{E_2 y_2^A + R_0 x_0^A}{E_2 + R_0} \qquad z_M^D = \frac{E_2 y_2^D + R_0 x_0^D}{E_2 + R_0}$$

3. Identify M on the plot



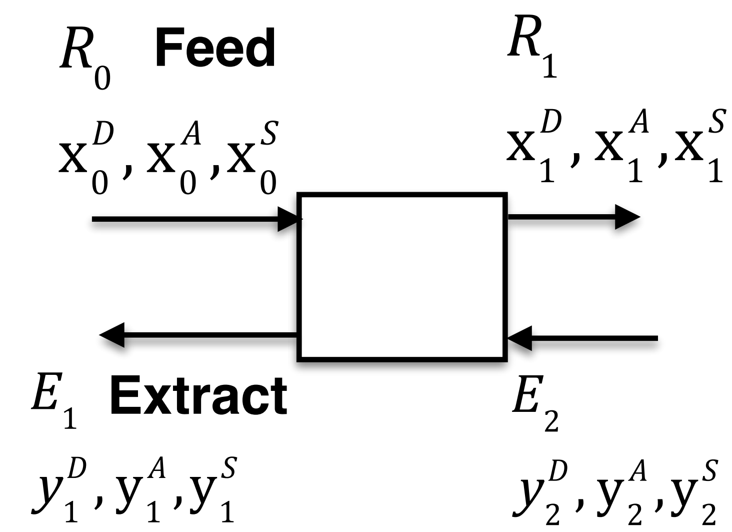
Single-stage extraction

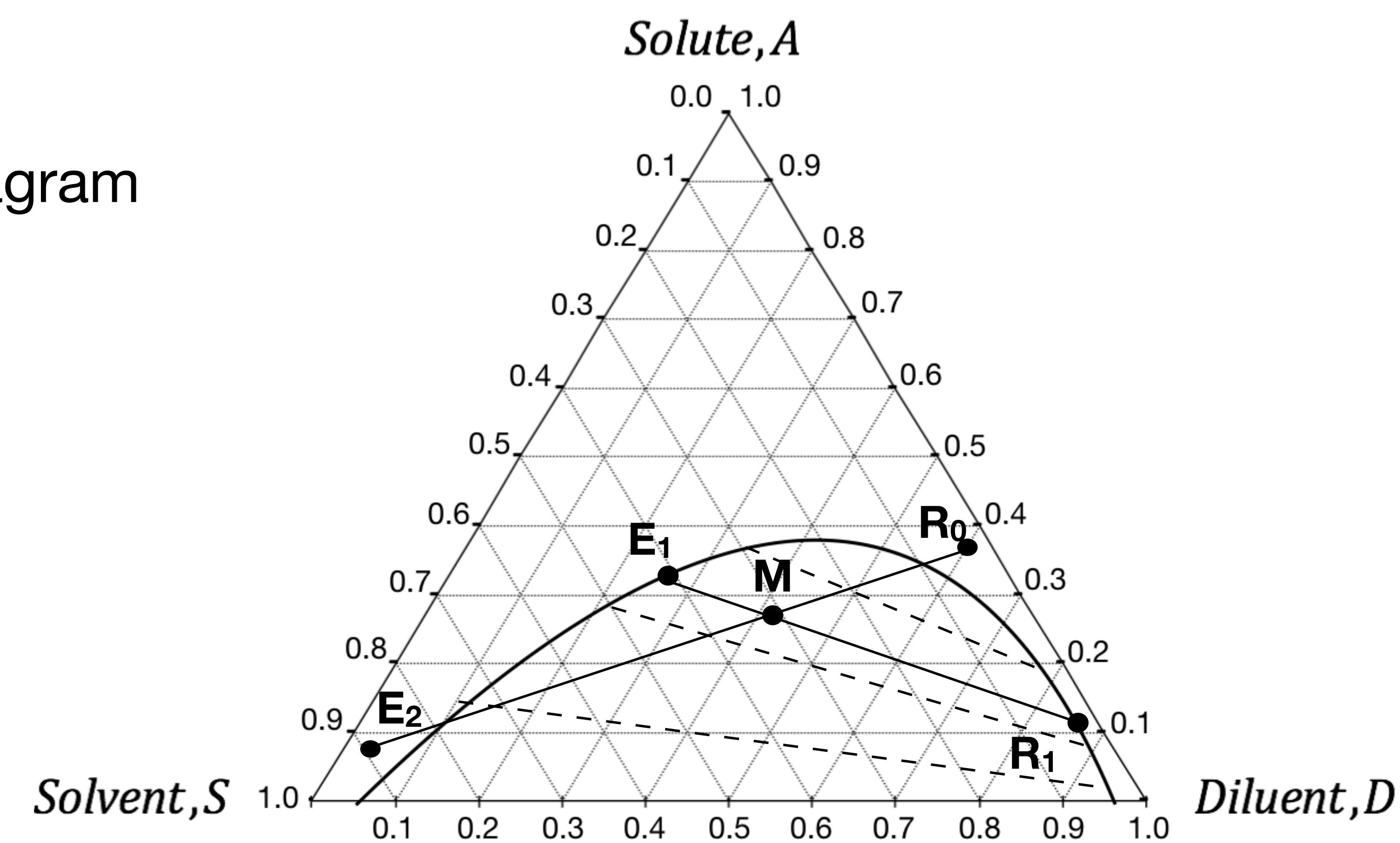
4. Exploit the fact that R_1 and E_1 are in equilibrium

5. R_1 and E_1 will be connected by tie-line and will pass through point M. Guiding tie lines are provided.

6. Calculated R_1 and E_1 using tie-lines.

7. Read $y_1^D, y_1^A, y_1^S, x_1^D, x_1^A, x_1^S$ from the diagram





Cross-flow

Specified

R_0 $\quad$ x_0^D, x_0^A, x_0^S

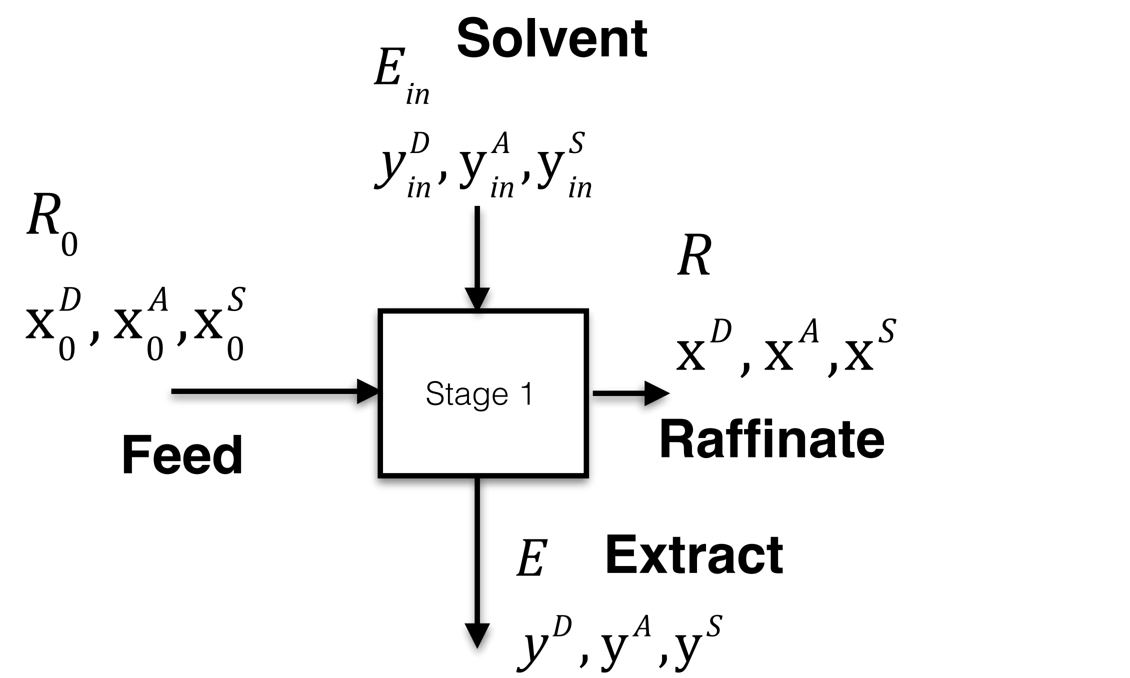
E_{in} $\quad$ $y_{in}^D, y_{in}^A, y_{in}^S$

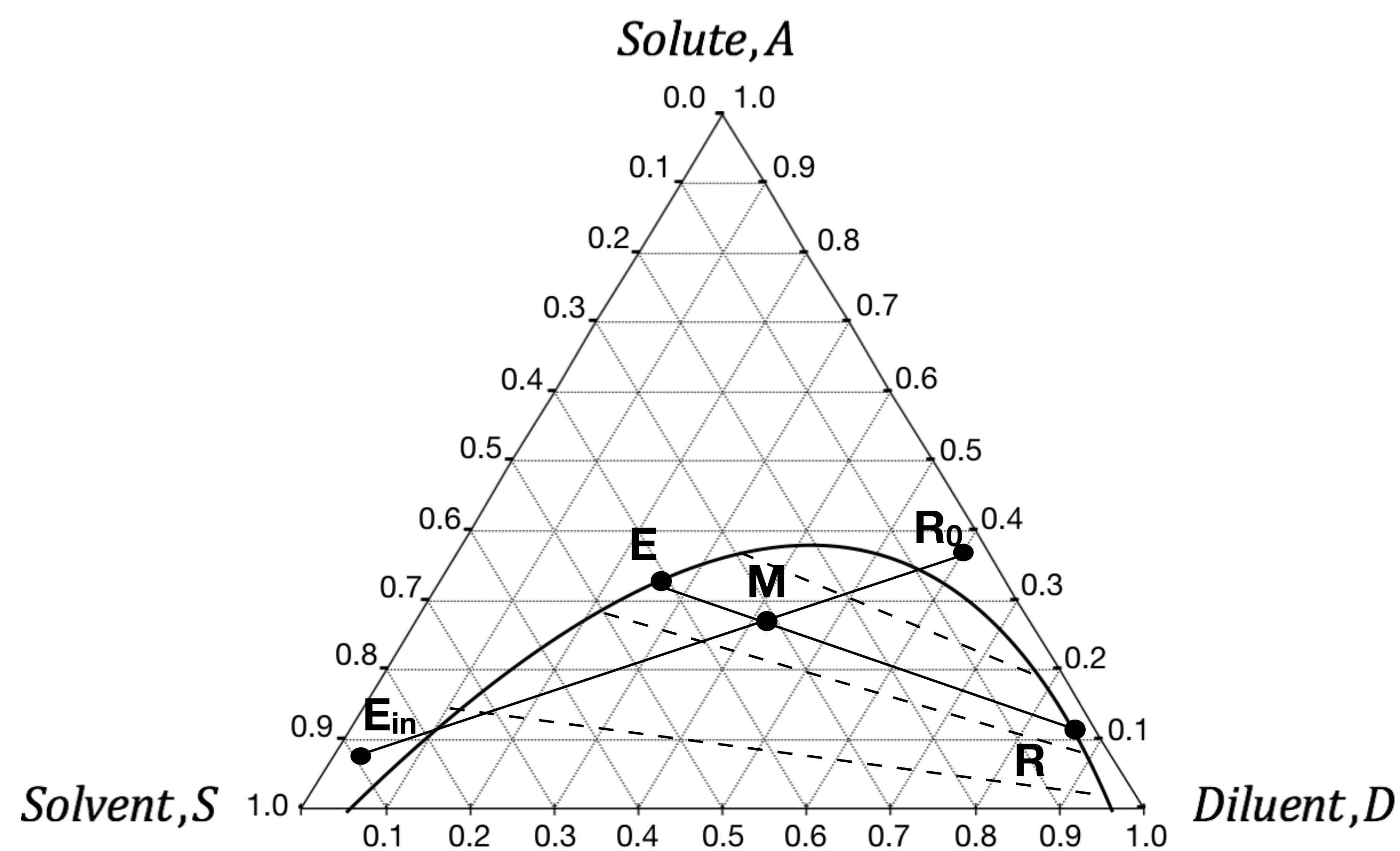
Need to calculate

R $\quad$ x^D, x^A, x^S

E $\quad$ y^D, y^A, y^S

No difference with the previous case





Two-stage cross-flow

Specified

R_0 $\quad x_0^D, x_0^A, x_0^S$

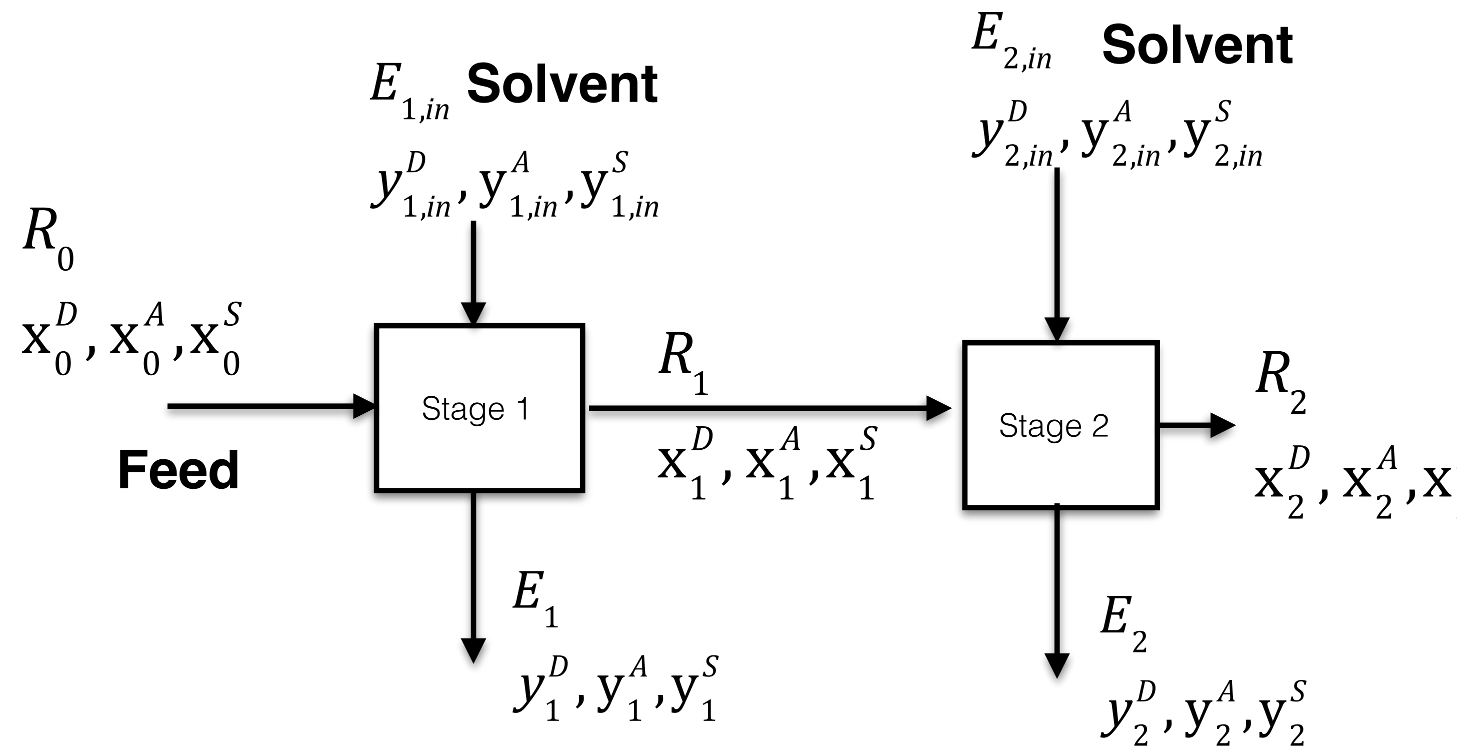
$E_{i,in}$ $\quad y_{i,in}^D, y_{i,in}^A, y_{i,in}^S$

Need to calculate

E_1 $\quad y_1^D, y_1^A, y_1^S$

E_2 $\quad y_2^D, y_2^A, y_2^S$

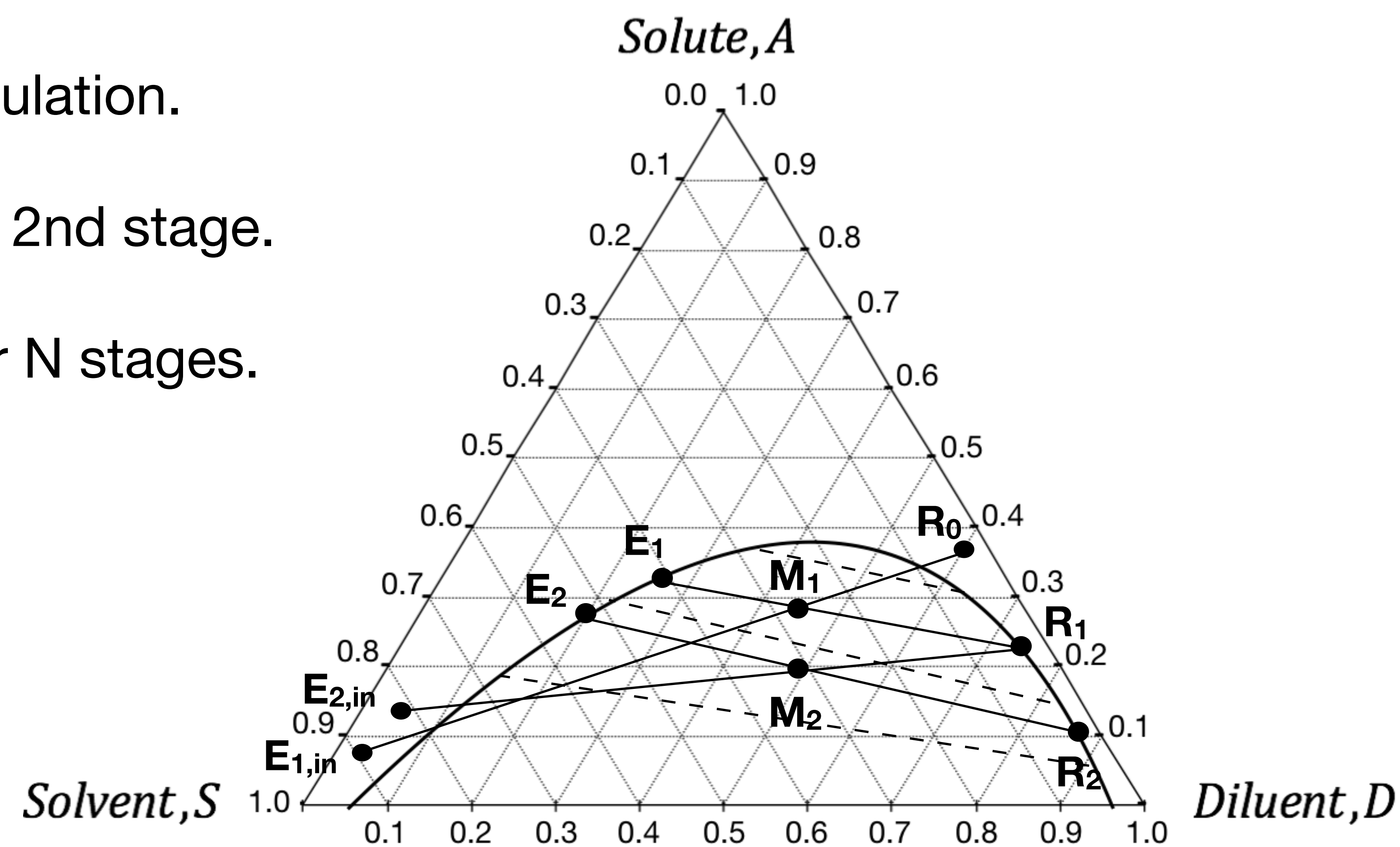
R_2 $\quad x_2^D, x_2^A, x_2^S$



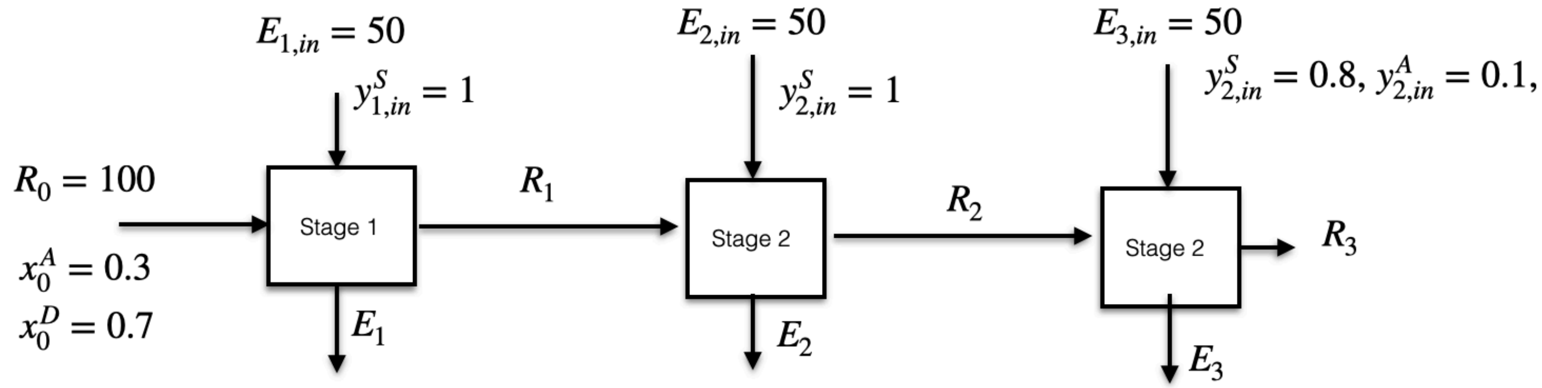
1. Carry out the first stage calculation.

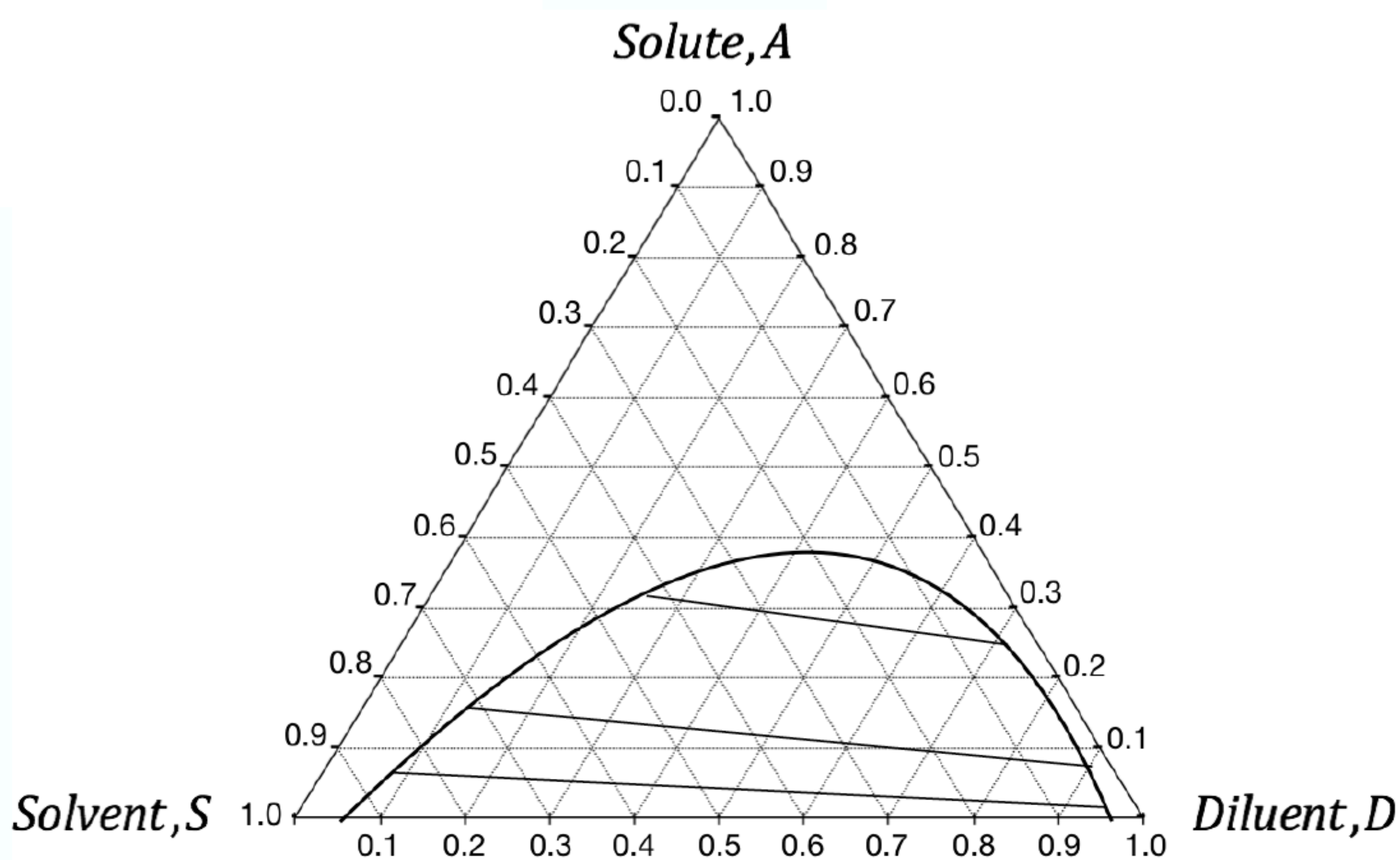
2. Use R_1 and $E_{2,in}$ as feeds for 2nd stage.

3. The process can be used for N stages.

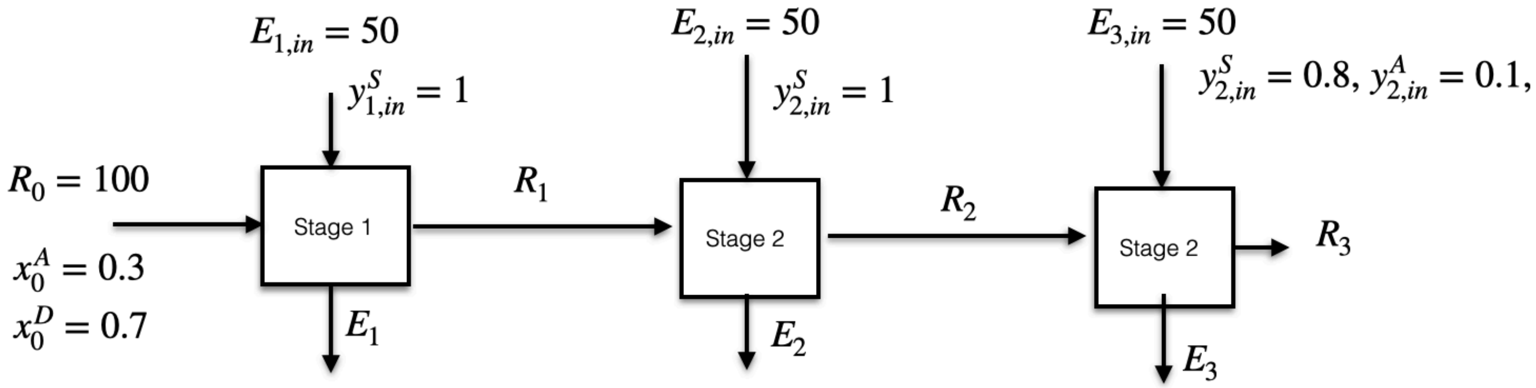


Calculate the amount of solute, A, left in the outlet raffinate stream R3.





Calculate the amount of solute, A, left in the outlet raffinate stream R_3.



$$Z^A_{M1} = \frac{E_{1,in}y^A_{1,in} + R_0x^A_0}{E_{1,in} + R_0}$$

$$Z^D_{M1} = \frac{E_{1,in}y^D_{1,in} + R_0x^D_0}{E_{1,in} + R_0}$$

$M_1 = 150$ $\quad z^A_{M1} = 0.2$ $\quad z^D_{M1} = 0.47$ $\quad$ Draw R_1E_1 as per other tie lines

$R_1 = 4.4/9.8 * 150 = 67.3$ $\quad x^A_1 = 0.15$ $\quad x^D_1 = 0.82$

(4.4 and 9.8 are distances measured by ruler)

Get M_2 by connecting R_1 with $E_{2,in}$

$M_2 = R_1 + E_{2,in} = 117.3$ $\quad z^A_{M2} = 0.086$ $\quad z^D_{M2} = 0.47$

Draw R_2E_2 as per other tie lines

$R_2 = 5.6/12.5 * 117.3 = 52.6$ $\quad x^A_2 = 0.05$ $\quad x^D_2 = 0.92$

(5.6 and 12.5 are distances measured by ruler)

Get M_3 by connecting R_2 with $E_{3,in}$ $\quad z^A_{M2} = 0.06$ $\quad z^D_{M2} = 0.52$

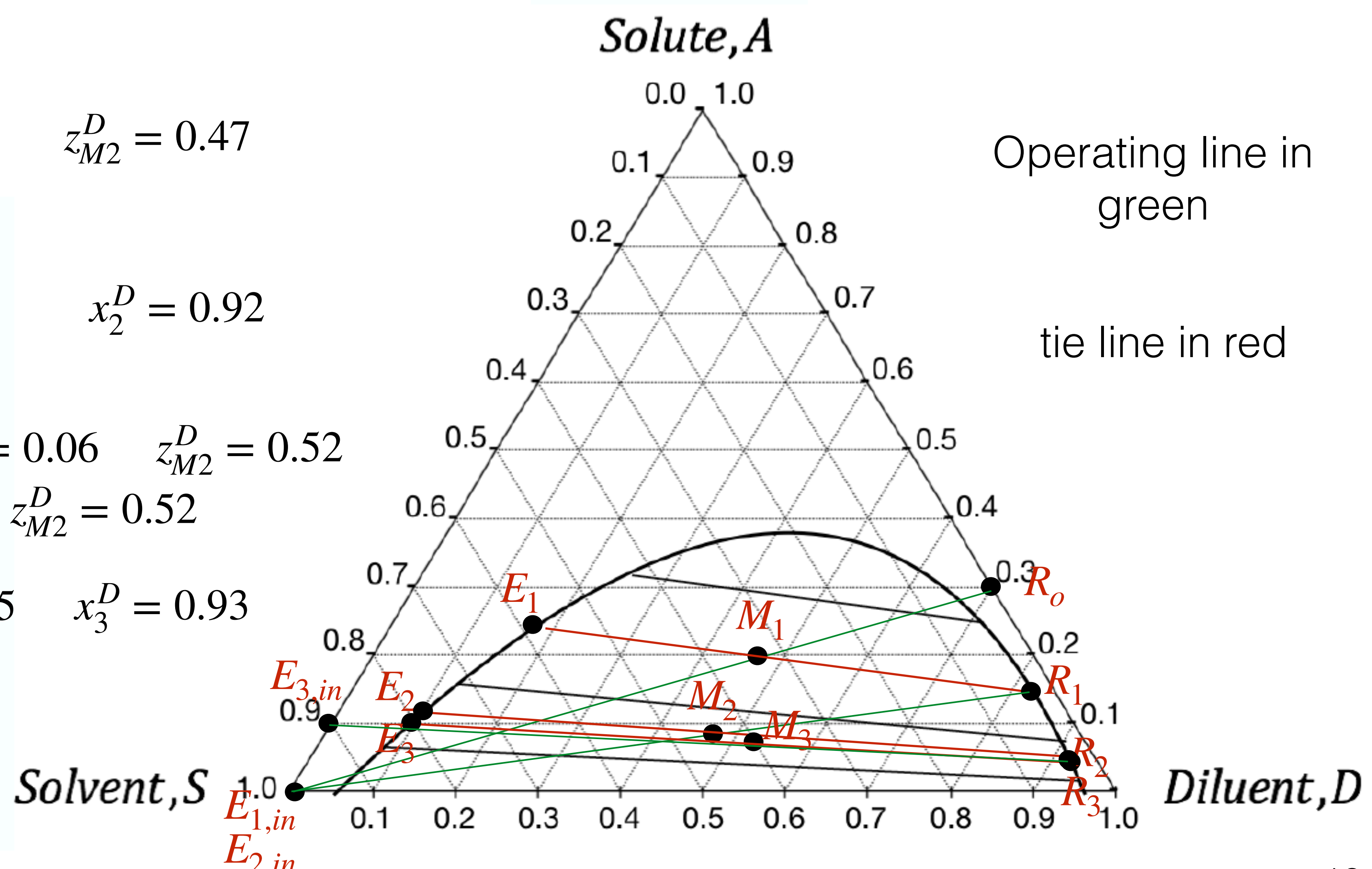
$M_3 = R_2 + E_{3,in} = 102.6$ $\quad z^A_{M2} = 0.07$ $\quad z^D_{M2} = 0.52$

R_3 composition is similar to R_2 $\quad x^A_3 = 0.05$ $\quad x^D_3 = 0.93$

E_3 composition is similar to $E_{3,in}$

$R_3 = 47$

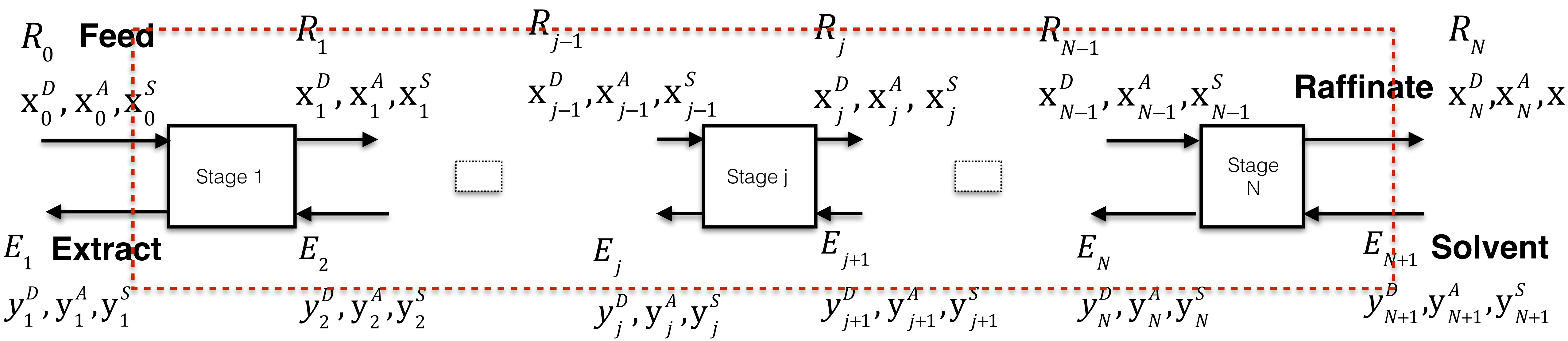
Third stage did not help much to purify



Operating line in green

tie line in red

Countercurrent extraction: overall balance



Overall balance

M is Hypothetical mixture

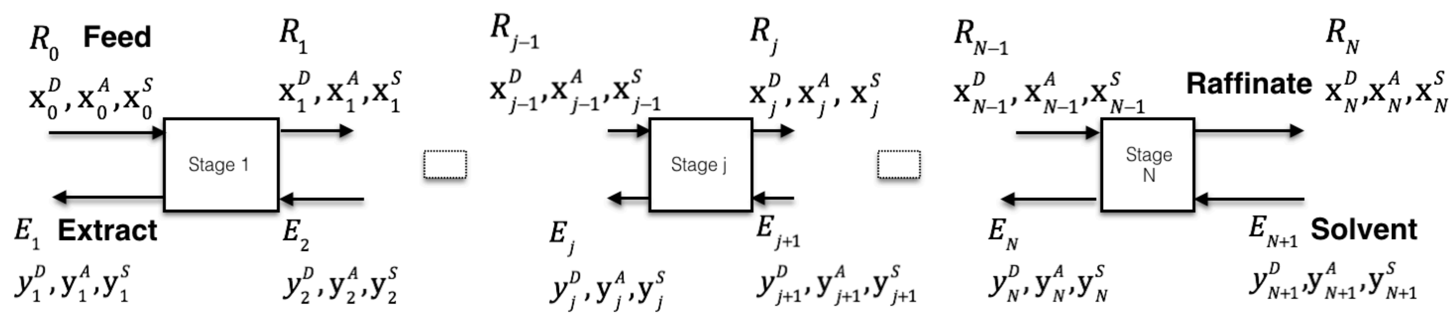
$$R_0 + E_{N+1} = R_N + E_1 \quad = M$$

$$R_0 x_0^A + E_{N+1} y_{N+1}^A = R_N x_N^A + E_1 y_1^A \quad = M z_M^A$$

$$R_0 x_0^D + E_{N+1} y_{N+1}^D = R_N x_N^D + E_1 y_1^D \quad = M z_M^D$$

R_N and E_1 are not at equilibrium!!

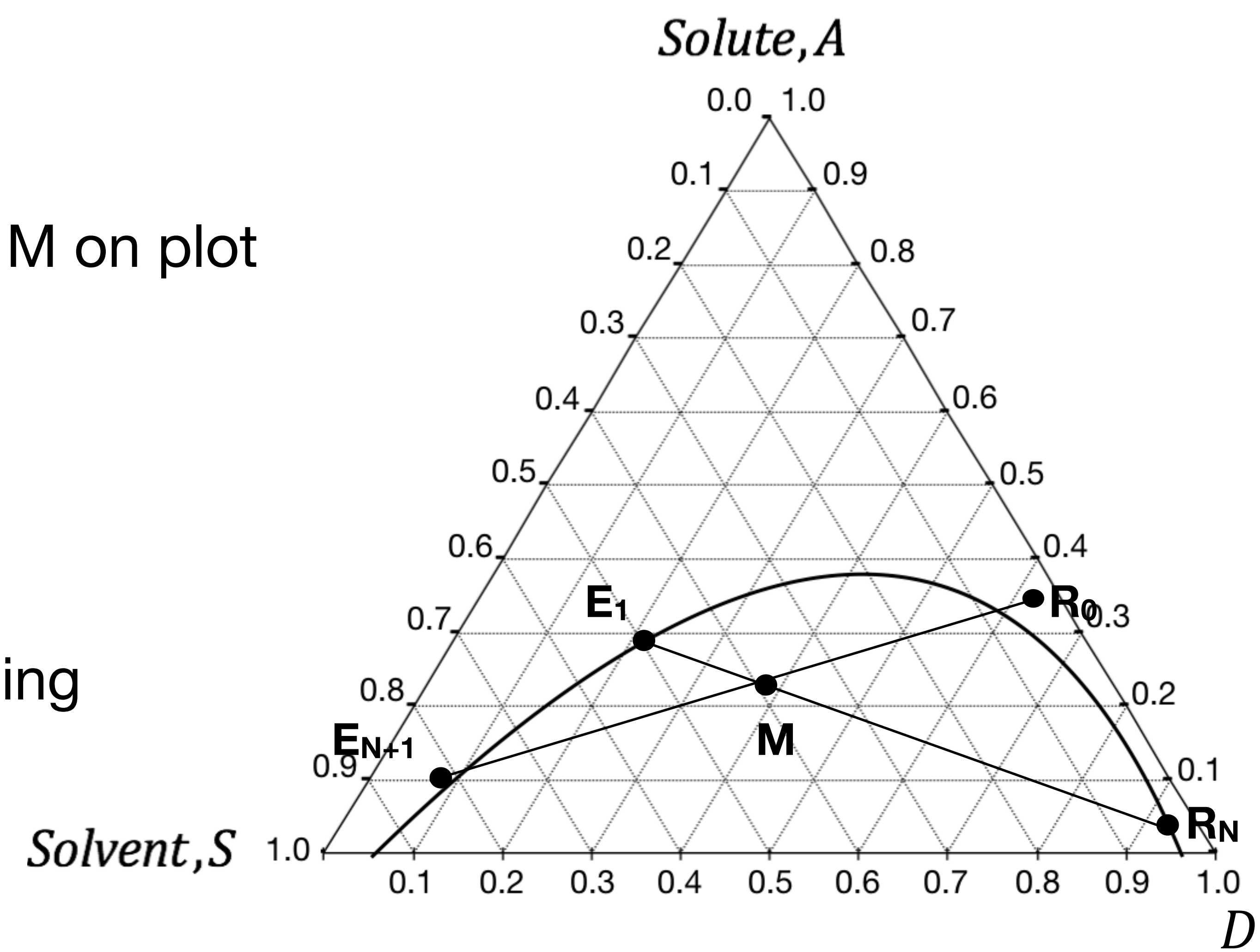
Countercurrent extraction: overall balance



$$z_M^A = \frac{E_{N+1} y_{N+1}^A + R_0 x_0^A}{E_{N+1} + R_0} = \frac{E_N y_N^A + R_1 x_1^A}{E_N + R_1}$$

$$z_M^D = \frac{E_{N+1} y_{N+1}^D + R_0 x_0^D}{E_{N+1} + R_0} = \frac{E_N y_N^D + R_1 x_1^D}{E_N + R_1}$$

Find M on plot

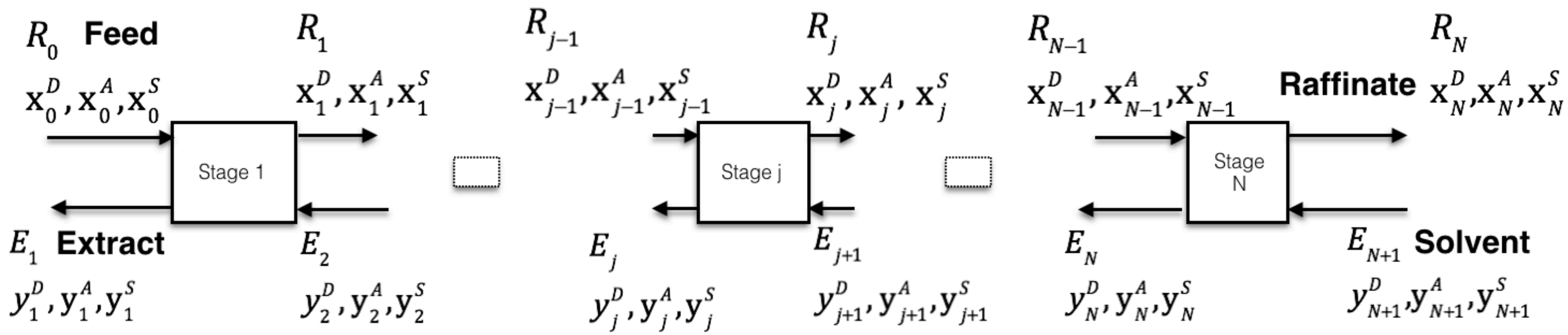


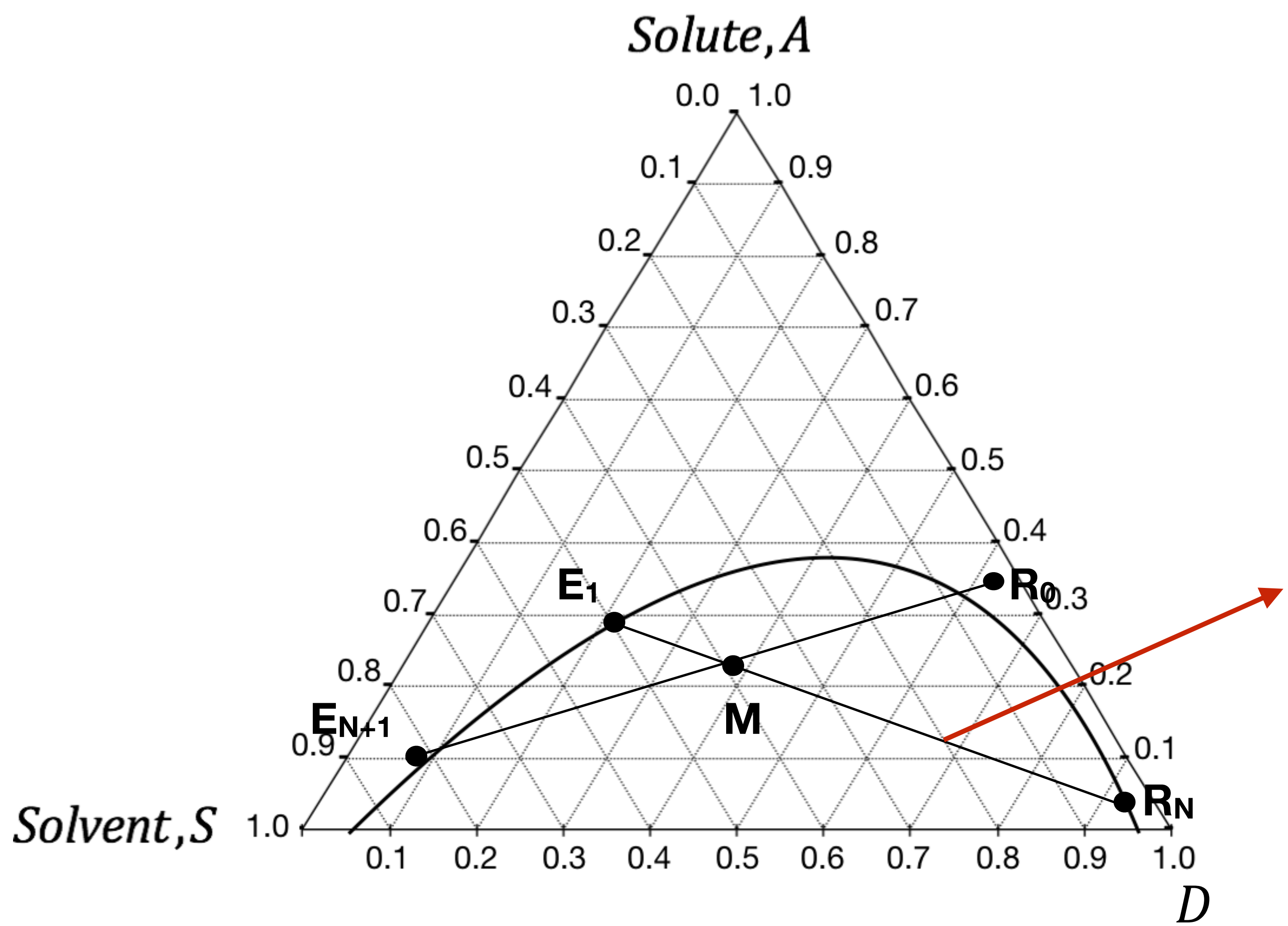
Point M lies at the intersections of lines joining

- E_{N+1} and R_0
- E_1 and R_N

So, if R_N is given then E_1 can be figured out.

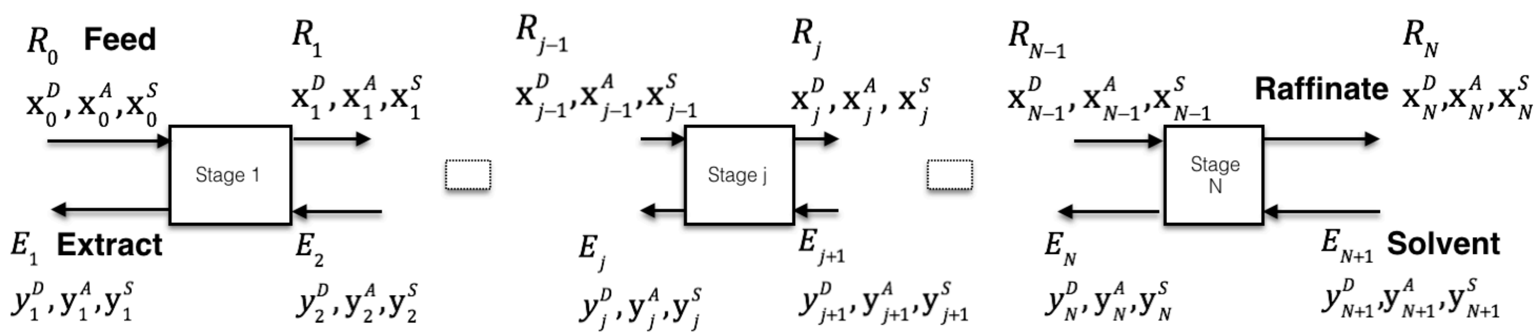
Why E_1 and R_N are on equilibrium curve?

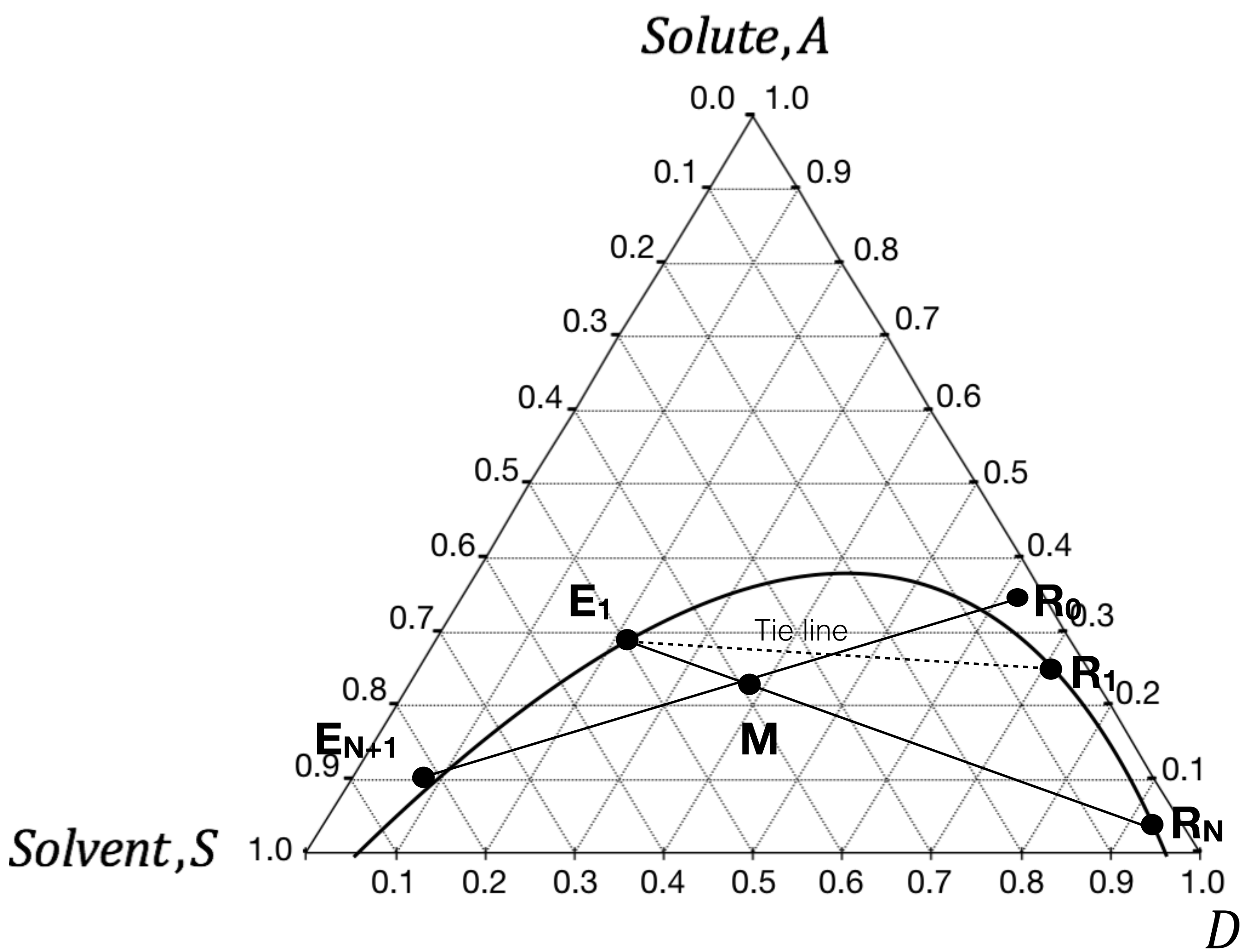




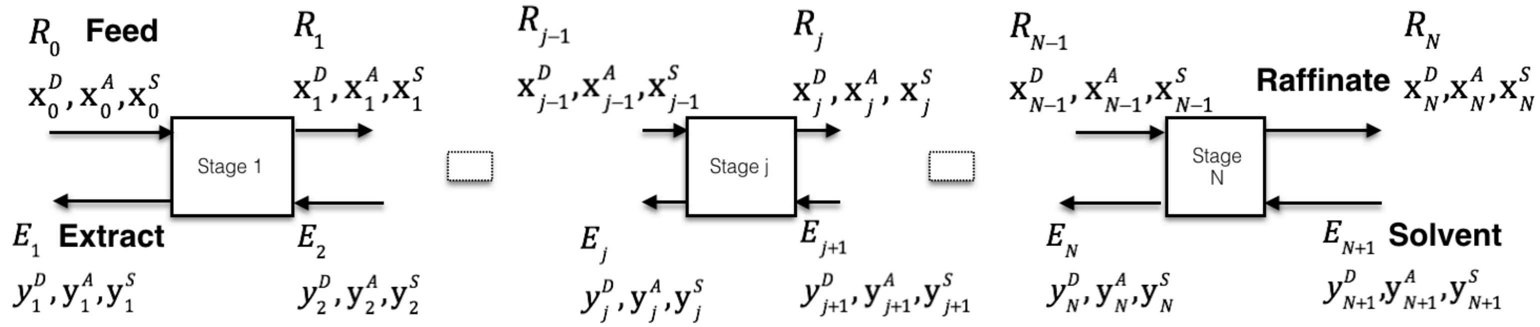
Is this a tie-line?

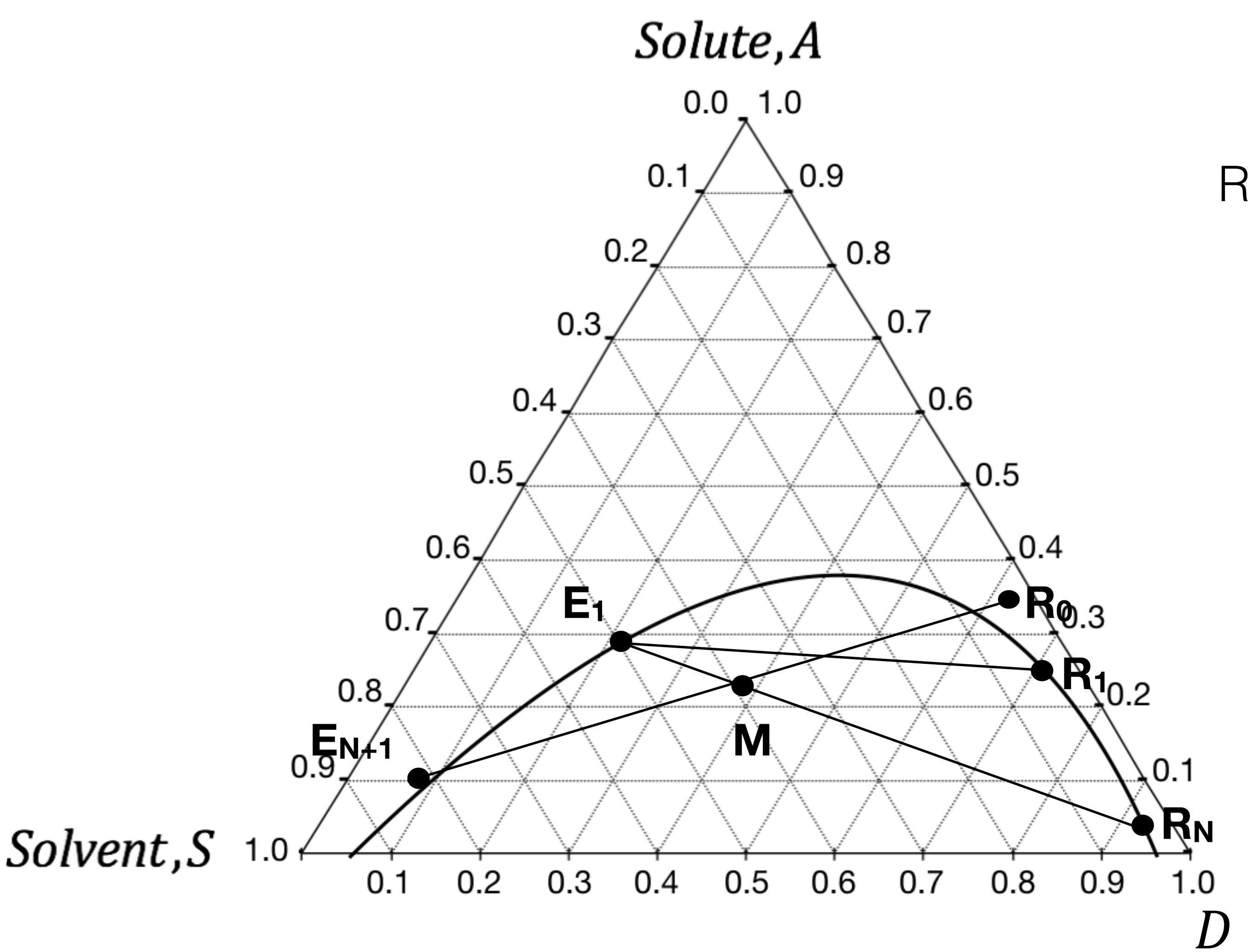
Can you identify position of R1?





How would you calculate number of stages? Can you identify position of E_2?





R_1 and E_2 are related by operating line

Trick to find E_2.

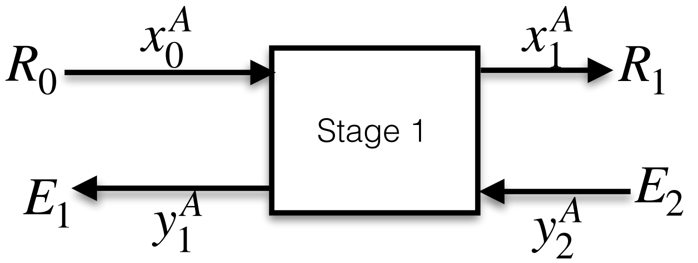
1. E_2 will lie on the equilibrium curve (in equilibrium with R_2) because it comes out from stage 2.
2. What if we had a fixed point Δ such that E_2 lies in a straight line that connects R_1 and Δ.

EPFL

Can you identify position of E_2? Lets find Δ

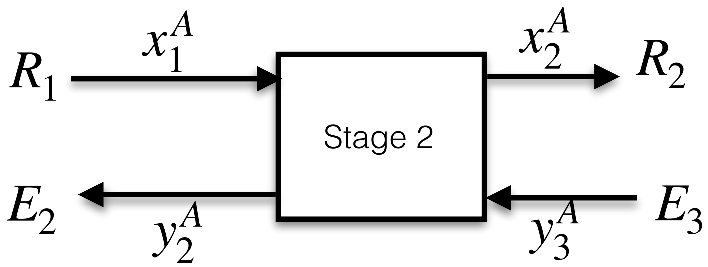
Stage 1 $\quad R_0 + E_2 = R_1 + E_1 \qquad \Rightarrow E_1 - R_0 = E_2 - R_1 = \Delta$

$$R_0 x_0^A + E_2 y_2^A = R_1 x_1^A + E_1 y_1^A \qquad E_1 y_1^A - R_0 x_0^A = E_2 y_2^A - R_1 x_1^A = \Delta z_\Delta^A$$



Stage 2 $\quad R_1 + E_3 = R_2 + E_2 \qquad \Rightarrow E_3 - R_2 = E_2 - R_1 = E_1 - R_0 = \Delta$

$$R_1 x_1^A + E_3 y_3^A = R_2 x_2^A + E_2 y_2^A \qquad \Rightarrow E_2 y_2^A - R_1 x_1^A = E_3 y_3^A - R_2 x_2^A = \Delta z_\Delta^A$$



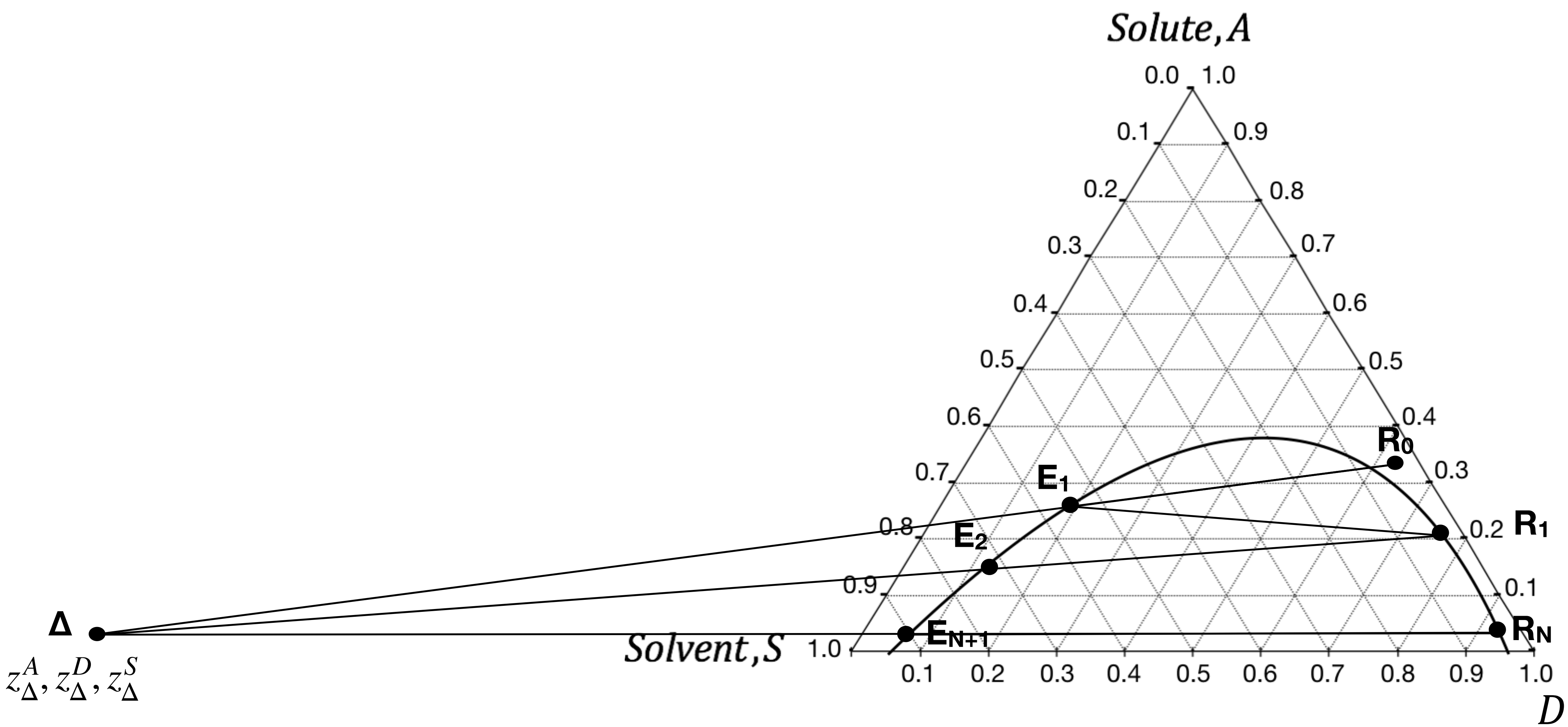
$$E_1 - R_0 = E_2 - R_1 = E_3 - R_2 = \Delta$$

$$\Rightarrow E_{j+1} - R_j = \Delta \qquad \Rightarrow E_{j+1} = \Delta + R_j$$

$$\Rightarrow E_{j+1} y_{j+1}^A = \Delta z_\Delta^A + R_j x_j^A \qquad \Rightarrow E_{j+1} y_{j+1}^D = \Delta z_\Delta^D + R_j x_j^D$$

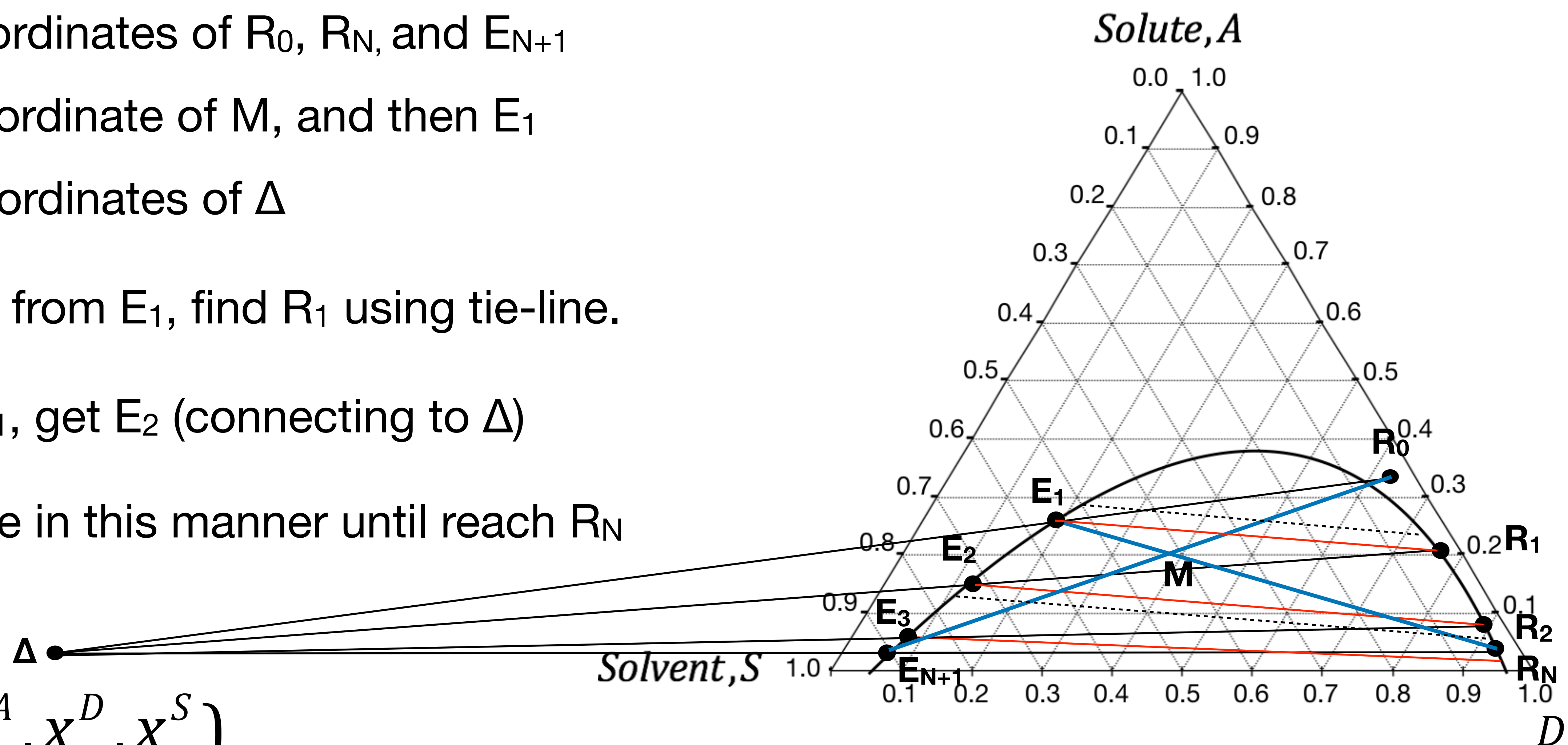
1. E_{j+1} is a mixture of composition at R_j and Δ
2. E_2 lies in a straight line that connects R_1 and Δ
3. Δ can be located using E_1 and R_0 and E_{N+1} and R_N

Can you identify position of E_2? Lets find Δ



Countercurrent extraction: Number of stages

- Plot coordinates of R_0, R_N, and E_{N+1}
- Find coordinate of M, and then E_1
- Find coordinates of Δ
- Starting from E_1, find R_1 using tie-line.
- From R_1, get E_2 (connecting to Δ)
- Continue in this manner until reach R_N



$(x_\Delta^A, x_\Delta^D, x_\Delta^S)$

N=3

EPFL