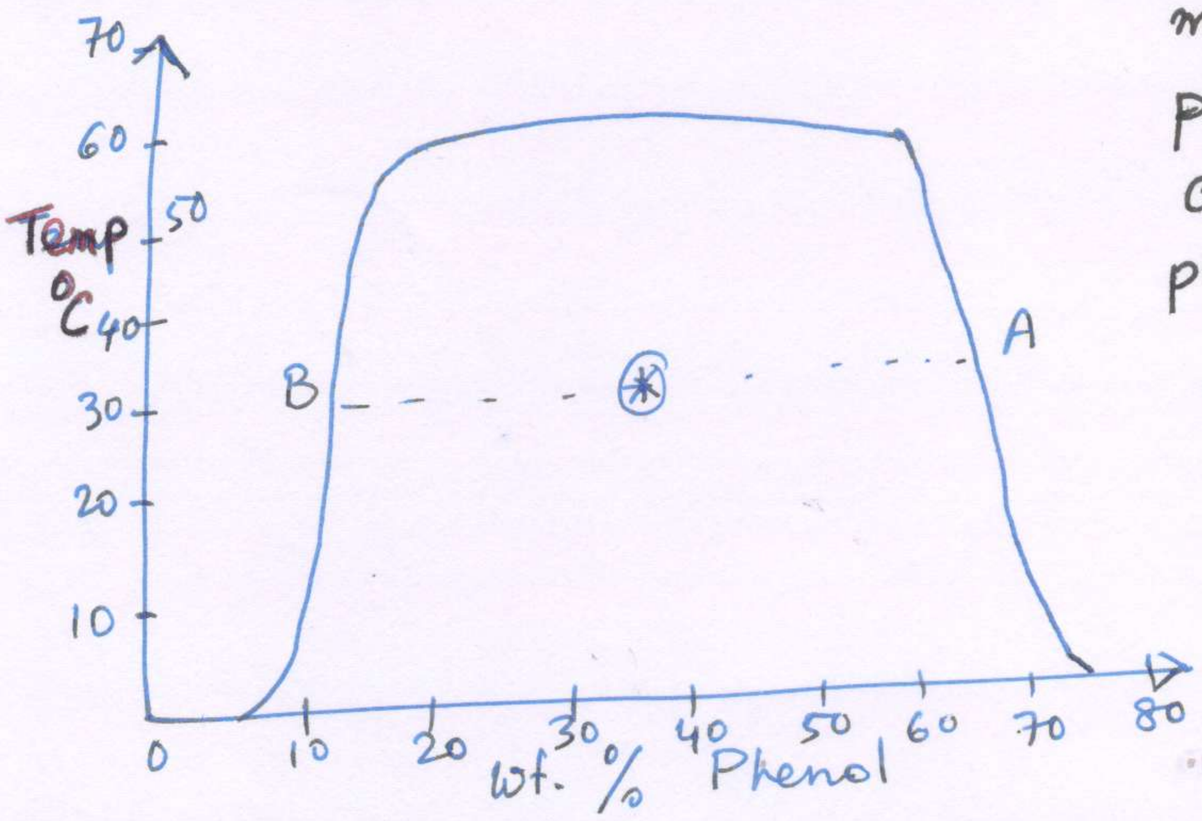
Partial Miscibility

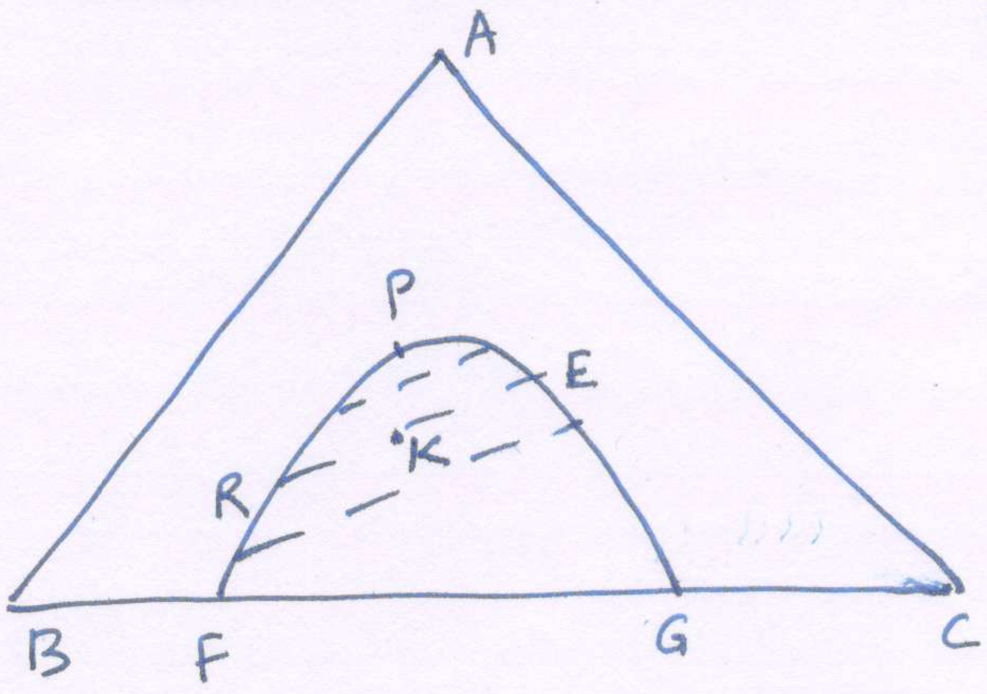
Solubility of Phenol in water



At a temperature of 50°C, mixture containing more than 11.8 % and less than 62.6 % phenol will separate into two layers containing 11.8 % phenol and 62.6 % phenol respectively.

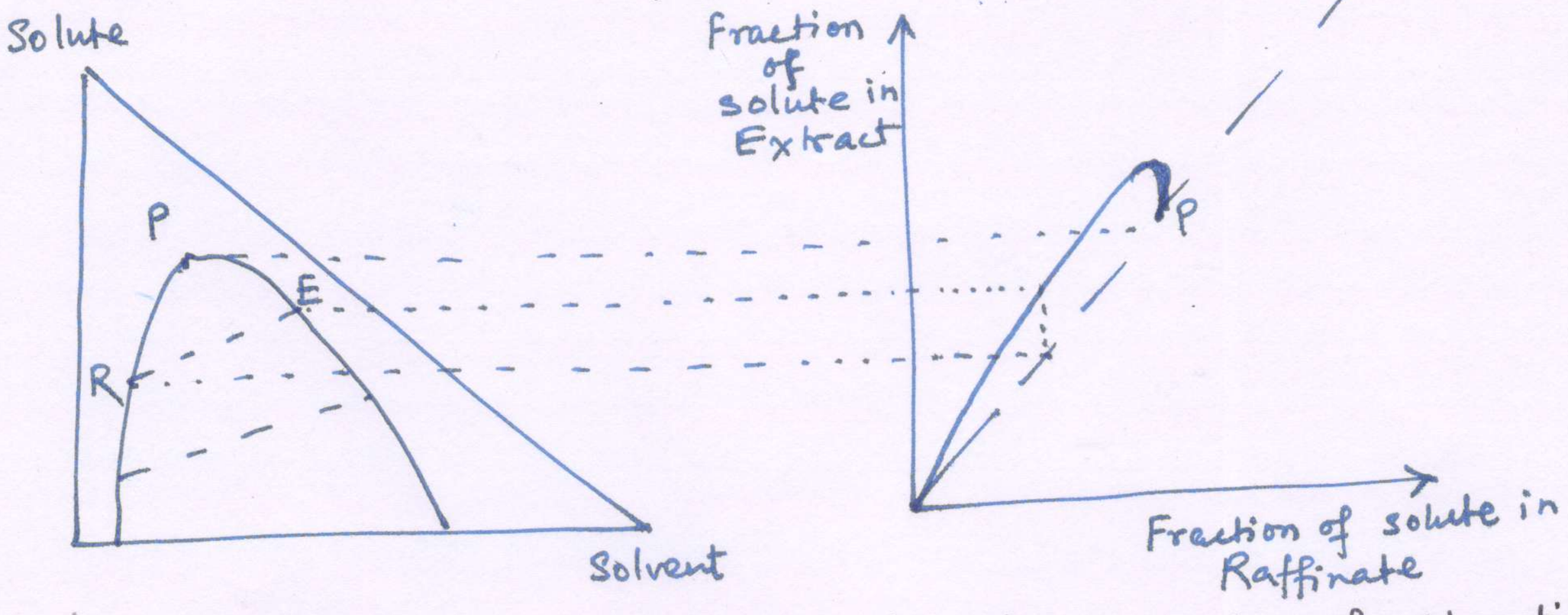
When the temperature of the same mixture is raised beyond 66°C, the mixture becomes homogeneous.

Ternary Liquid Mixtures



Below FPG is the region of immiscibility.
A mixture of composition K will separete into two phases of compositions E and R respectively.

$$\frac{\text{Mass of Phase E}}{\text{Mass of Phase R}} = \frac{KR}{KE}$$



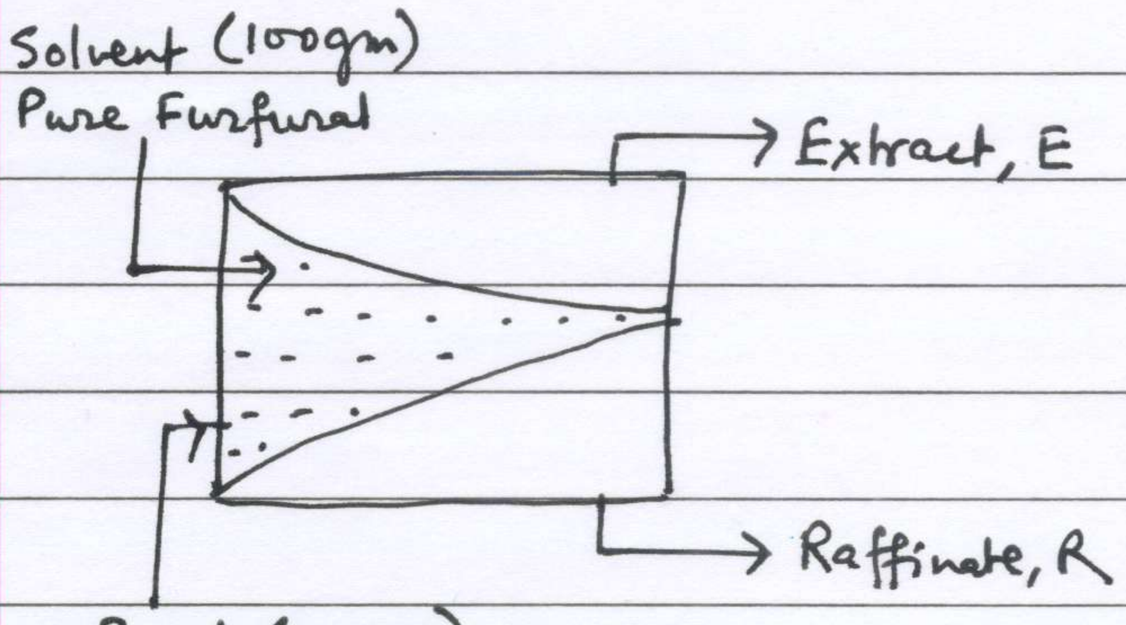
- Use of Extraction in competition with other mass transfer operation
- Choice of Solvent
- Effect of temperature
- Equipment used for extraction
- Extraction limit

Equilibrium Miscibility Data in wt.% @ 25°C, 101 kPa (No vapor phase existing at this condition)

Furfural	Ethylene Glycol	Water
94.8	0.0	5.2
84.5	11.4	4.1
63.1	29.7	7.2
49.4	41.6	9.0
33.8	50.1	16.1
20.1	50.5	29.4
9.2	28.1	62.7
7.9	0	92.1

Tie line Data

Glycol in aqueous layer (wt.%)	Glycol in organic layer (wt.%)
49.1	49.1
32.1	48.8
11.5	41.8
7.7	28.9
6.1	21.9
4.8	14.3
2.3	7.3



Q1. Feed solution is contacted with its own weight of pure furfural solvent at 25°C and 101 kPa.

(i) Calculate the composition of equilibrium extract and raffinate phases.

(ii) Calculate the composition of water-glycol mixture obtained by removing all of the furfural from the extract.

Q2. For the same chemical system, Consider Feed flowrate of 250 kg/h containing 24 %. glycol and rest water, contacted in counter current multi-stage mode with 100 kg/h of pure furfural as the solvent stream. If the solute% in raffinate has to be brought down to 2.5% glycol, calculate the number of stages.

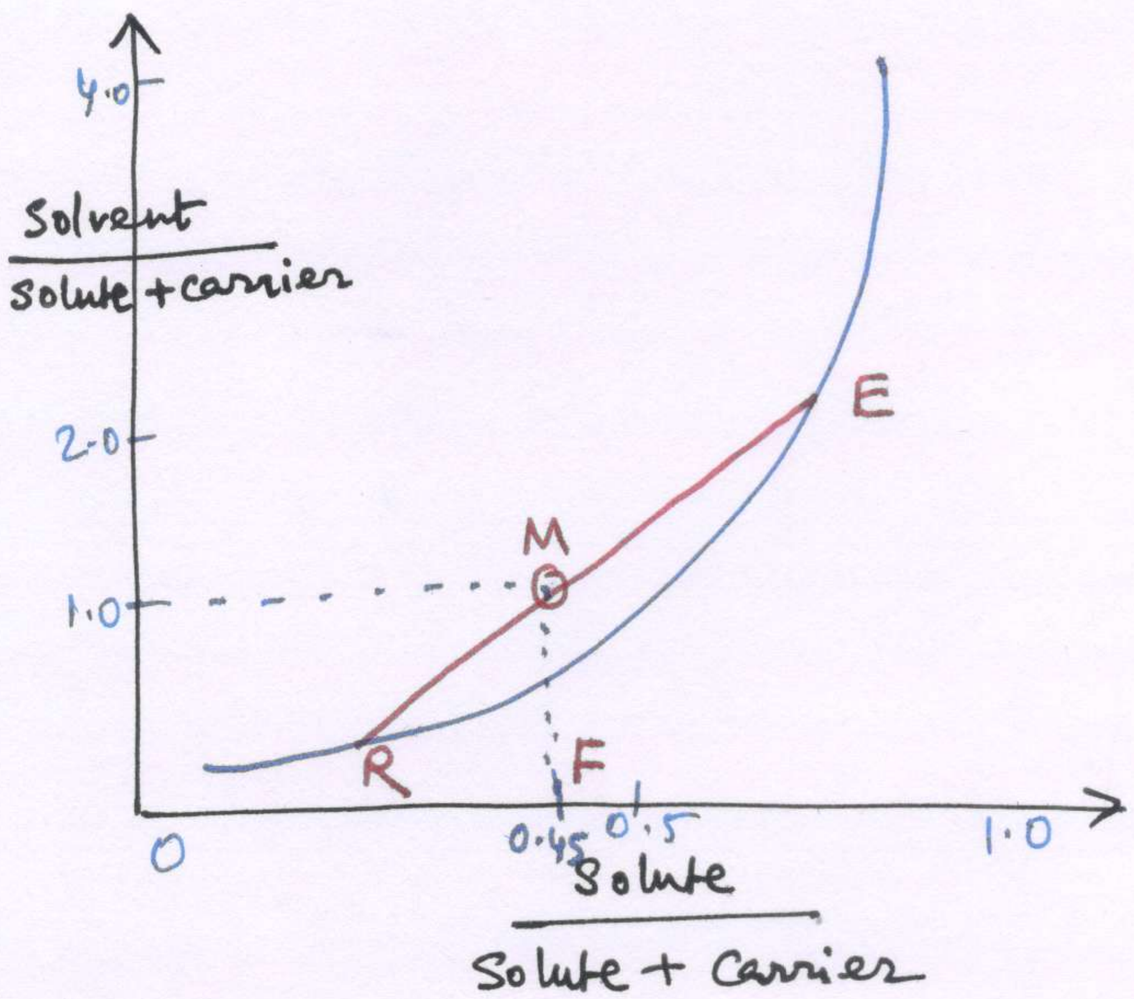
Answer to Question 1

E: (27.9% Solute, 6.5% carrier, 65.6 % solvent)

R: (8% solute, 84% carrier, 8% solvent)

Solvent-free extract composition: (83% solute, 17% Carriers, 0% solvent)

Janecke Diagram (solvent-free method)



F and M will be on one vertical line

Since $\frac{\text{Solute}}{\text{Solute + carrier}}$ remains the same.

Since feed is contacted with its own weight of pure solvent,

$\left(\frac{\text{Solvent}}{\text{Feed}}\right)$ will be 1.0.

Coordinates of E : (0.81, 1.91)

Coordinates of R : (0.09, 0.09)

If Z^E = Total mass of components (solute + carrier) in the extract

Z^R = Total mass of components (solute + carrier) in the raffinate

Furfural (Solvent) Balance : $1.91\ Z^E + 0.09\ Z^R = 100$

Glycol (Solute) Balance : $0.81\ Z^E + 0.09\ Z^R = 45$

$\Rightarrow Z^E = 50$ gm, $Z^R = 50$ gm

Solvent (Furfural) in the extract $= 1.91\ Z^E = 95.5$ gm

Solvent in the raffinate $= 0.09\ Z^E = 4.5$ gm

Solute (Glycol) in the extract $= 0.81\ Z^E = 40.5$ gm

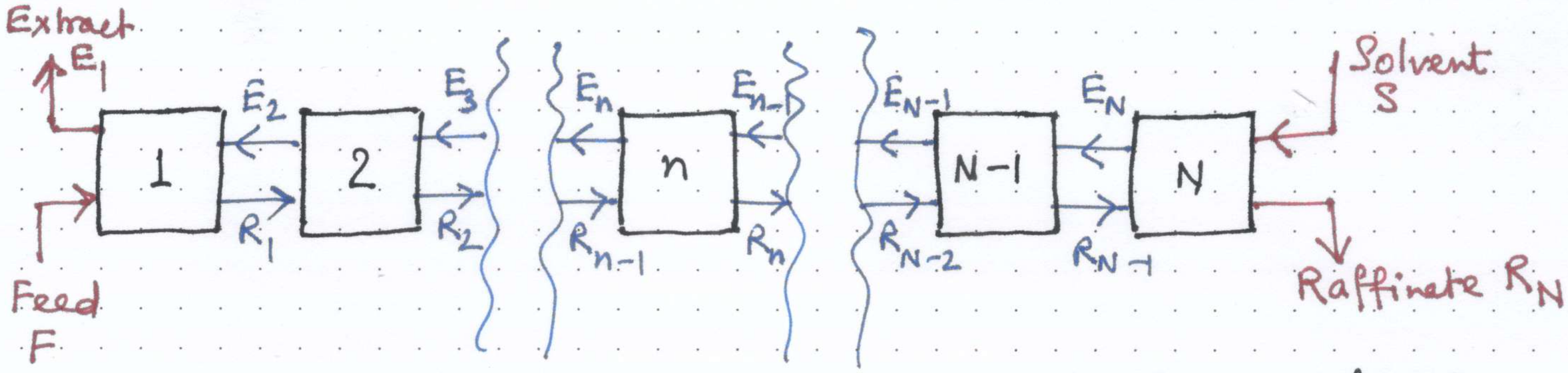
Solute in the raffinate $= 0.09\ Z^R = 4.5$ gm

Carrier (Water) in the extract $= 50 - 40.5 = 9.5$ gm

Carrier in the raffinate $= 50 - 4.5 = 45.5$ gm

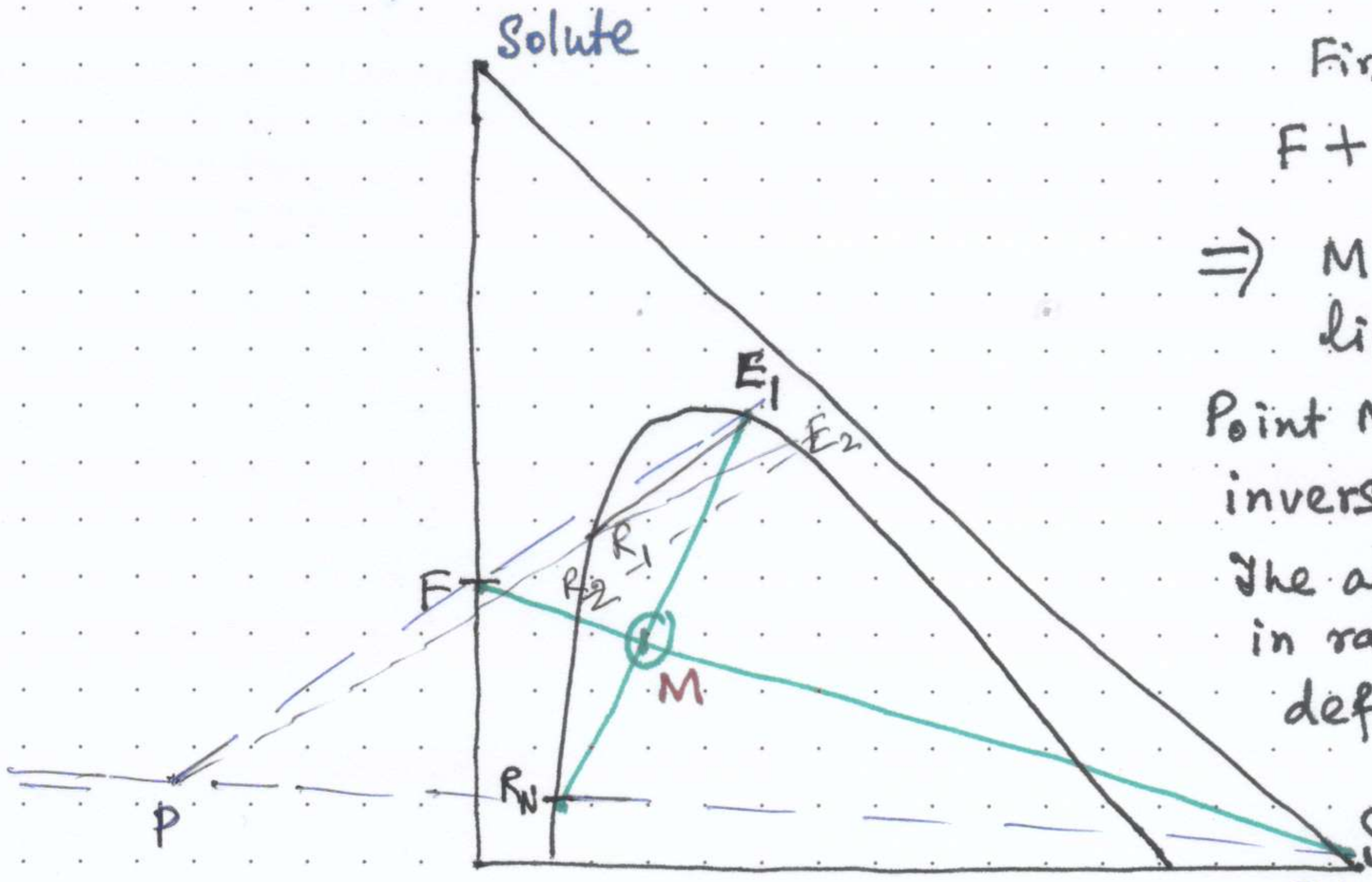
Total wt. of extract $= 95.5 + 40.5 + 9.5 = 145.5$ gm

Total wt. of raffinate $= 4.5 + 4.5 + 45.5 = 54.5$ gm



Material balances around groups of stages from the feed end are

$$F - E_1 = \cdots\cdots = R_{n-1} - E_n = \cdots = R_N - S = P \quad \text{(say)} \qquad \text{---- Eq. 1}$$



Firstly, from Eq. 1

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

$\Rightarrow$ M will lie on both $\overline{FS}$ and $\overline{E_1 R_N}$ lines.

Point M is located on FS line by inverse lever arm rule.

The admissible concentration of solute in raffinate is specified, which defines the position of R_N.

$\overline{R_N M}$ extended cuts the miscibility envelop at E_1.

Further from Eq. 1

$$\left.\begin{aligned} F &= E_1 + P \\ R_N &= S + P \end{aligned}\right\} \Rightarrow \left.\begin{aligned} &F \text{ lies on } \overline{E_1 P} \text{ line} \\ &R_N \text{ lies on } \overline{SP} \text{ line} \end{aligned}\right\} \Rightarrow P \text{ is the intersection point of } \overline{R_N S} \text{ extended and } \overline{F E_1} \text{ extended lines.}$$

// Cutting of stages / stepping of stages to find No. of equilibrium stages reqd.

// Limits of S/F ratio

Solution of Q. 2

$M = F + S = 250 + 100 = 350$ kg

If solute is referred as 'A', solvent as 'S', and carrier as 'C'

$$(x_A)_M M = (x_A)_F F + (x_A)_S S = 0.24(250) + 0(100) = 60 \text{ kg}$$

$$(x_A)_M = \frac{60}{350} = 0.171 \; ; \qquad \text{Similarly, } (x_C)_M = \frac{190 \text{ kg}}{350 \text{ kg}} \; ; \; (x_S)_M = \frac{100}{350}$$

Further,

$$(x_A)_M M = 60 = (x_A)_{R_N} R_N + (x_A)_{E_1} E_1$$

and $R_N + E_1 = F + S = M$

$(x_A)_{R_N}$ and $(x_A)_{E_1}$ can be obtained from the plot. Two equations for two unknowns give R_N, E_1

Alternatively, $\frac{E_1}{M} = \frac{\overline{MR_N}}{\overline{E_1 R_N}}$ and $\frac{R_N}{M} = \frac{\overline{ME_1}}{\overline{E_1 R_N}}$ can be used to find E_1 and R_N from the plot.

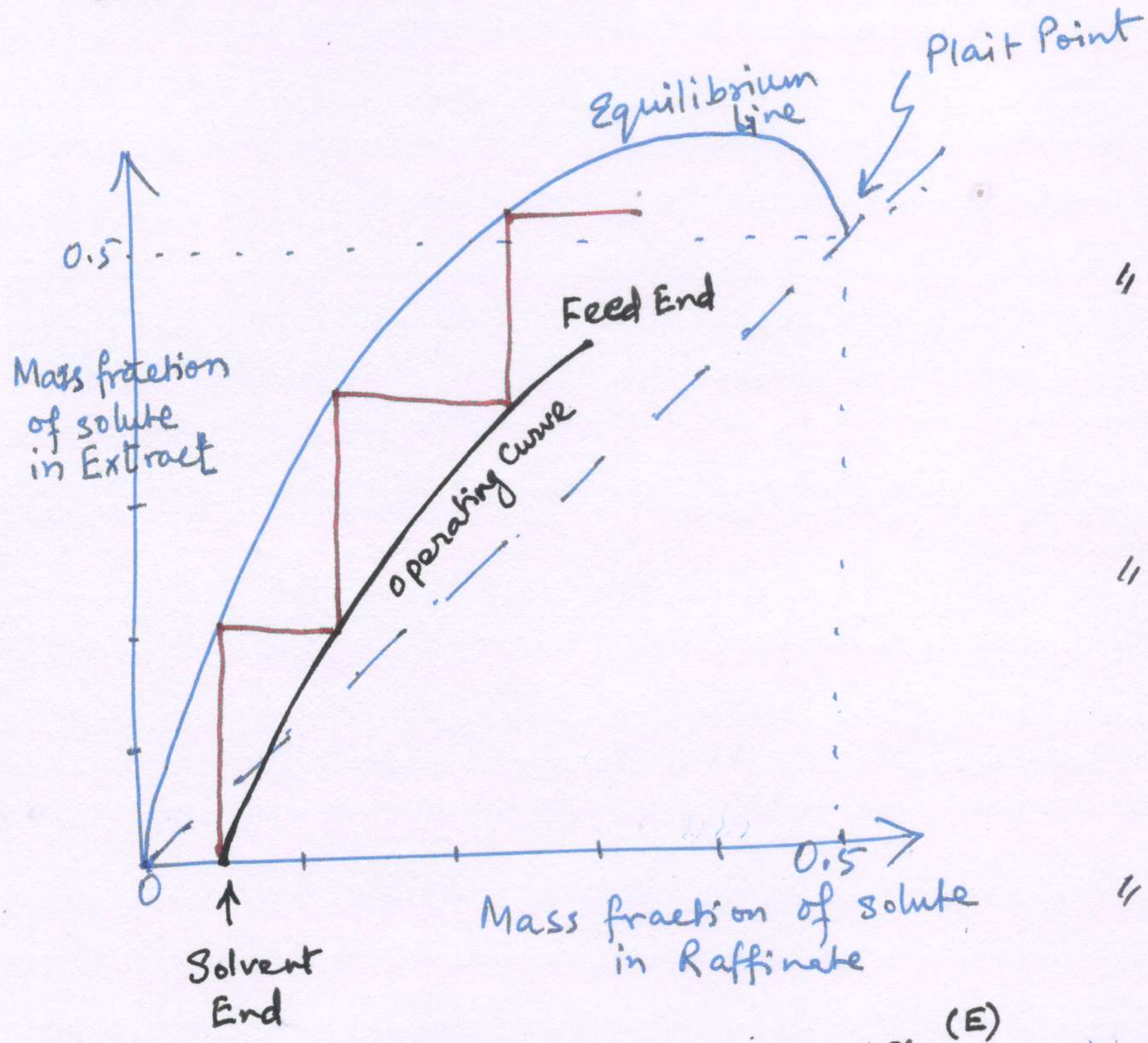
Solution of Q 2 contd.

$(x_A)_{R_N} = 0.025$ $\quad (x_A)_{E_1} = 0.365$ $\quad R_N = 198\ kg$

$(x_C)_{R_N} = 0.90$ $\quad (x_C)_{E_1} = 0.075$ $\quad E_1 = 152\ kg$

$(x_S)_{R_N} = 0.075$ $\quad (x_S)_{E_1} = 0.560$ $\quad$ No. of Stages:

Use of Auxiliary Distribution Curve



" A tieline in the triangular diagram refers to a point on the curve in the distribution diagram.

" On the ternary diagram, the arbitrary lines drawn from the difference (operating point) intersects the miscibility envelop

" Each arbitrary line intersects the miscibility envelop at two points giving a set of mass fractions of solute for extract and raffinate sides respectively.

" These mass fractions constitute the operating curve.

Distribution coefficient $K = \dfrac{x_i^{(E)}}{x_i^{(R)}}$ is stored and recalled using some database handler.

Conventional models for activity coefficient (e.g., NRTL, UNIQUAC) are used most commonly, since $K_{D_i} = \dfrac{\gamma_{i_L}^{(R)}}{\gamma_{i_L}^{(E)}}$

For example, (NRTL) $\ln \gamma_i = \dfrac{\sum_{j=1}^{c} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{c} G_{ki} x_k} + \sum_{j=1}^{c} \left[\dfrac{x_j G_{ij}}{\sum_{k=1}^{c} G_{kj} x_k} \left(\tau_{ij} - \dfrac{\sum_{k=1}^{c} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{c} G_{kj} x_k} \right) \right]$

where $G_{ji} = e^{-\alpha_{ji} \tau_{ji}}$

$\tau_{ij} = \dfrac{g_{ij} - g_{jj}}{RT}$

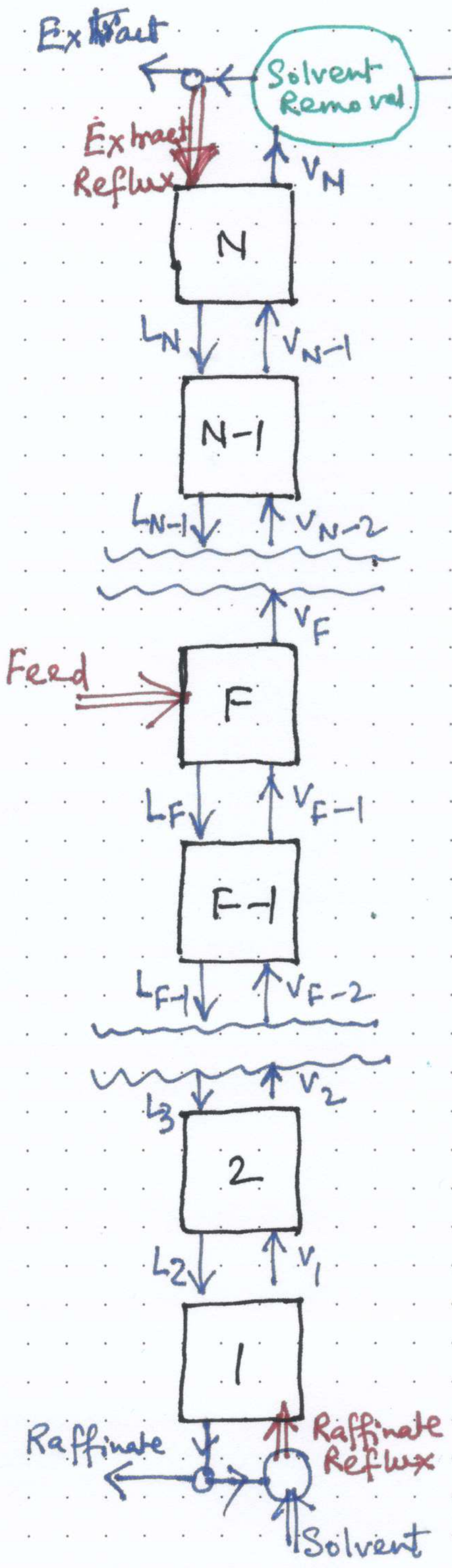
$\tau_{ji} = \dfrac{g_{ji} - g_{ii}}{RT}$

$G_{ii} = G_{jj} = 1$

$\tau_{ii} = \tau_{jj} = 0$

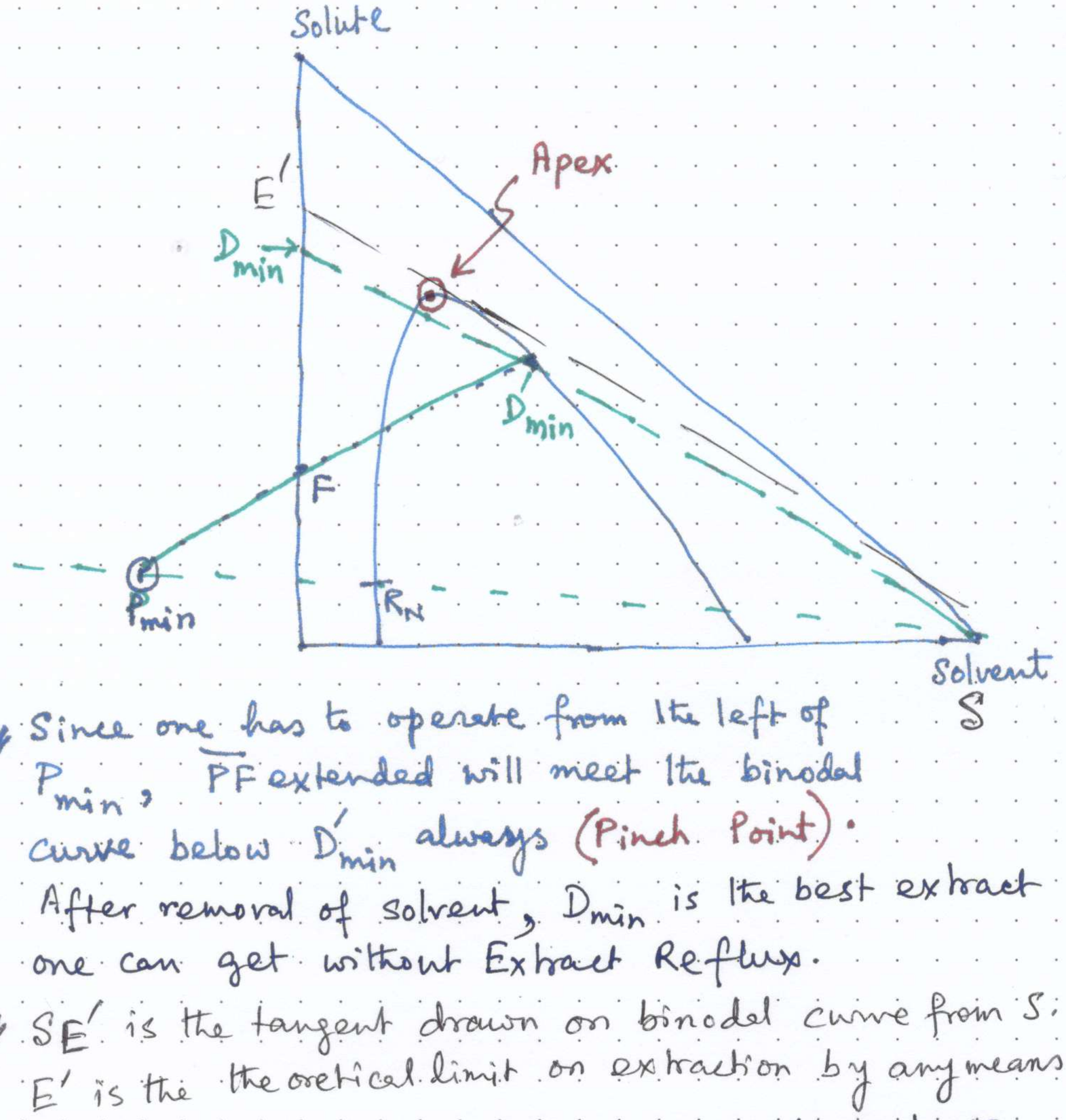
The parameters g_{ij}, g_{jj}, α_{ji} etc. can be regressed using the experimental data to store the value of Distribution coefficient.

Extract and Raffinate Reflux



// In simple counter-current extraction, the final extract stream V_N is removed from the same stage to which the feed stream is admitted.

// The purity of V_N gets restricted when feed has low concentration, since V_N and L_N have to be in equilibrium.



// Since one has to operate from the left of P_{min}, $\overline{PF}$ extended will meet the binodal curve below D'_{min} always (Pinch Point).

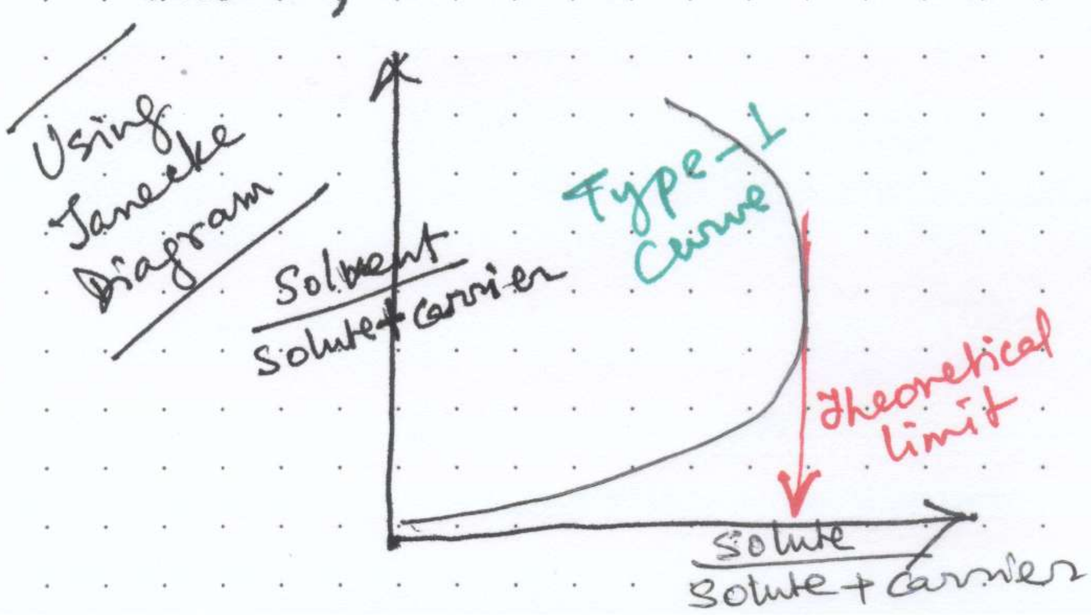
After removal of solvent, D_{min} is the best extract one can get without Extract Reflux.

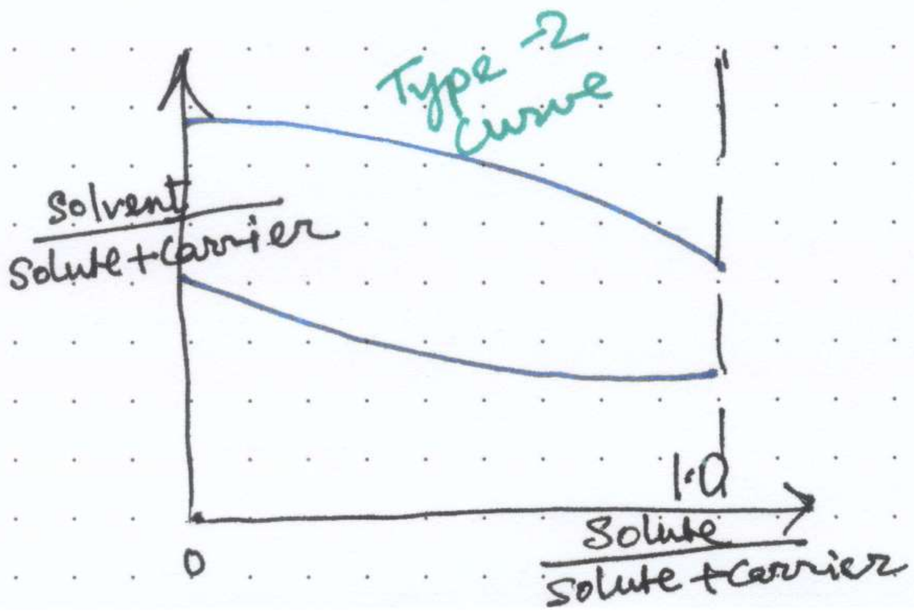
// SE' is the tangent drawn on binodal curve from S. E' is the theoretical limit on extraction by any means

// Through extract reflux, one can approach peak or apex of the binodal curve.

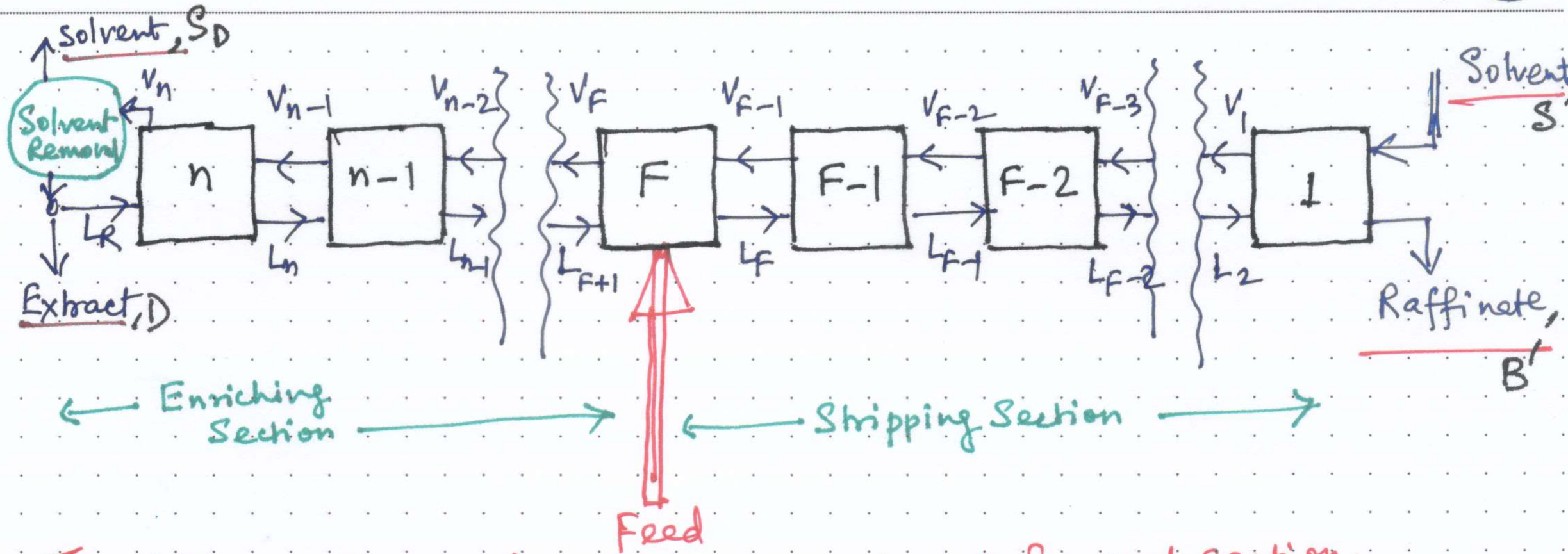
// Depending on the shape of binodal curve, apex can be above D'_{min}. In that case, purer extract is possible through extract reflux.

// Extract reflux works the best for Type-2 or near Type-2 miscibility curve, where theoretical limit is 100% solute in feed.





Extract Reflux



Two difference (operating) point is required, one for each section.

In the enriching section, $P' = V_n - L_R = V_{n-1} - L_n = \cdots = D + S_D$

= total flow leaving the extract end of the cascade. ···(Eq.1)

By overall material balance,

$$M = F + S = B' + D + S_D = B' + P' \quad \cdots \text{(Eq.2)}$$

Eq.1 implies P' will lie on $V_n L_R$ line where L_R is of same composition of V_n with solvent removed.

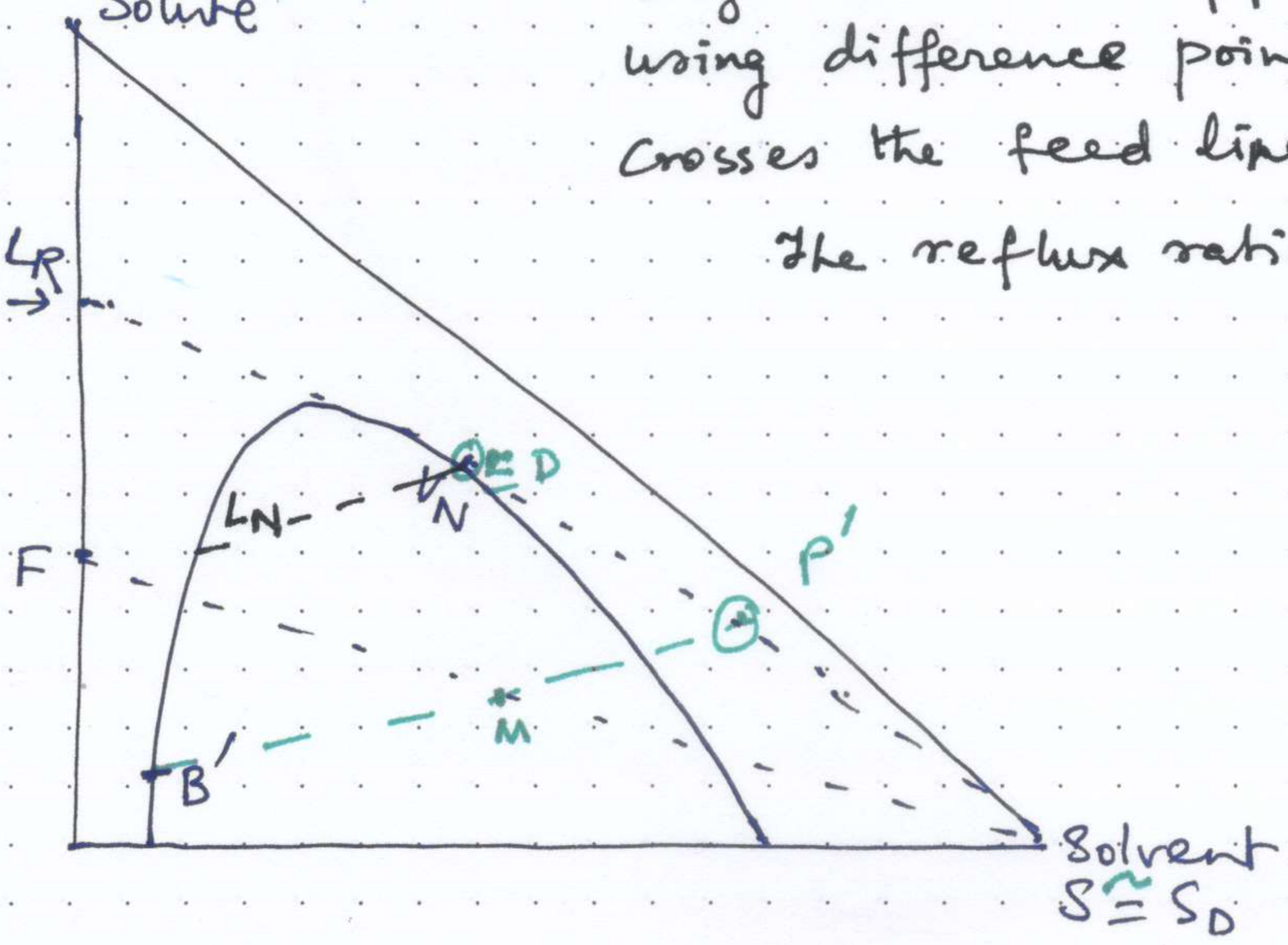
Eq.2 implies P' will lie on $B'M$ extended

$\Rightarrow$ P' will be at the intersection of the above two lines.

In the stripping section

$$P'' = B' - S = F - D - S_D = F - P'$$

$\Rightarrow$ P'' will be at the intersection of $\overline{FP'}$ and $\overline{B'S}$



Stages can be stepped off by starting from V_n and using difference point P' until an operating line crosses the feed line $\overline{FP'}$.

The reflux ratio $= \dfrac{V_n - D}{D} = \dfrac{L_R + S_D}{D}$

$$= \left(\frac{\overline{DP'}}{\overline{S_D P'}}\right)\left(\frac{\overline{L_R S_D}}{\overline{L_R D}}\right)$$

(By Mixing Rule)

Equilibrum Stages on Janecke Diagram

for Type-II System (Extract Reflux)

Solvent-free material Balance:

$$Y = \frac{\text{mass of solvent}}{\text{Mass of solvent-free liquid phase}}$$

$$X = \frac{\text{mass of solute}}{\text{Mass of solvent-free liquid phase}}$$

V_N = Mass of non-solvent in stream V_N

L_R, D, S_D etc. are mass of non-solvent in respective streams.

For solvent difference balance around a section of top stages, located above

Stage F

$$Y_{V_N} V_N - Y_D L_R = Y_{V_{N-1}} V_{N-1} - Y_{L_N} L_N = Y_{V_{N-2}} V_{N-2} - Y_{L_{N-1}} L_{N-1} = \cdots\cdots$$

$$= P'(V_N - L_R) = P'D \quad \cdots\cdots \text{Eq. 3}$$

$$\Rightarrow P' = Y_D + \frac{S_D}{D}$$

For non-solvent

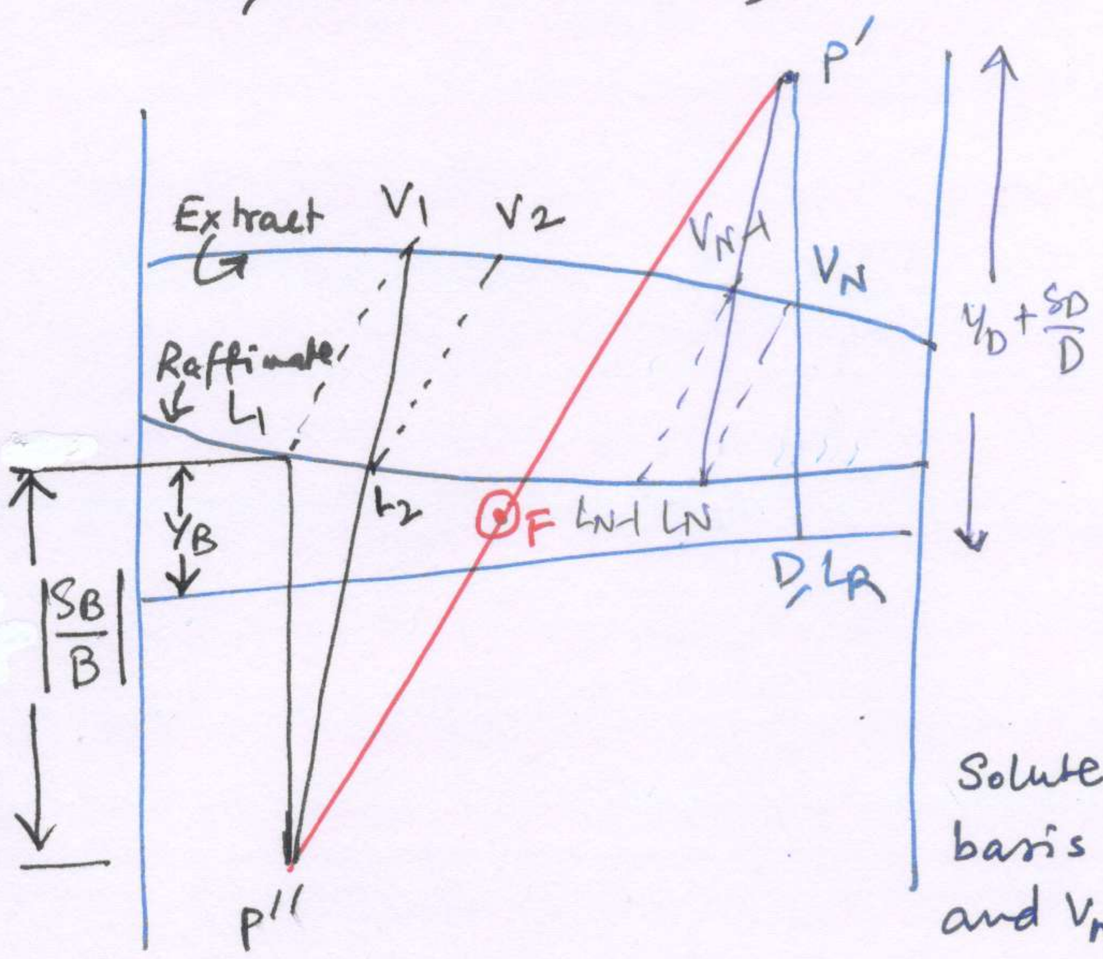
$$V_N - L_R = D \quad \cdots\cdots \text{Eq. 1}$$

(4^{th} stream is pure solvent)

For solvent

$$Y_{V_N} V_N - Y_D L_R = S_D + Y_D D \quad \cdots\cdots \text{Eq. 2}$$

(S_D: Solvent removed.)



Since in Janecke diagram, the y-axis is $\frac{\text{Solvent}}{\text{solvent-free material}}$, unlike the y-axis in ternary diagram, so to cancel the denominator, P' is multiplied by extract without the solvent.

Similarly,

$$P'' = Y_B - \frac{S_B}{B}$$

Solute compositions of D, L_R, and V_N on solvent-free basis are identical $\Rightarrow$ operating line through L_R and V_N is a vertical line passing through P'.

Stages are stepped off in a manner analogous to triangular diagram, starting from either the extract, D, or the raffinate B, alternating between operating lines and tie lines.

The transition from the enriching section (where P' is used) to the stripping section (where P'' is used) is made when an equilibrium tie line for a stage crosses the line $P'P''$.