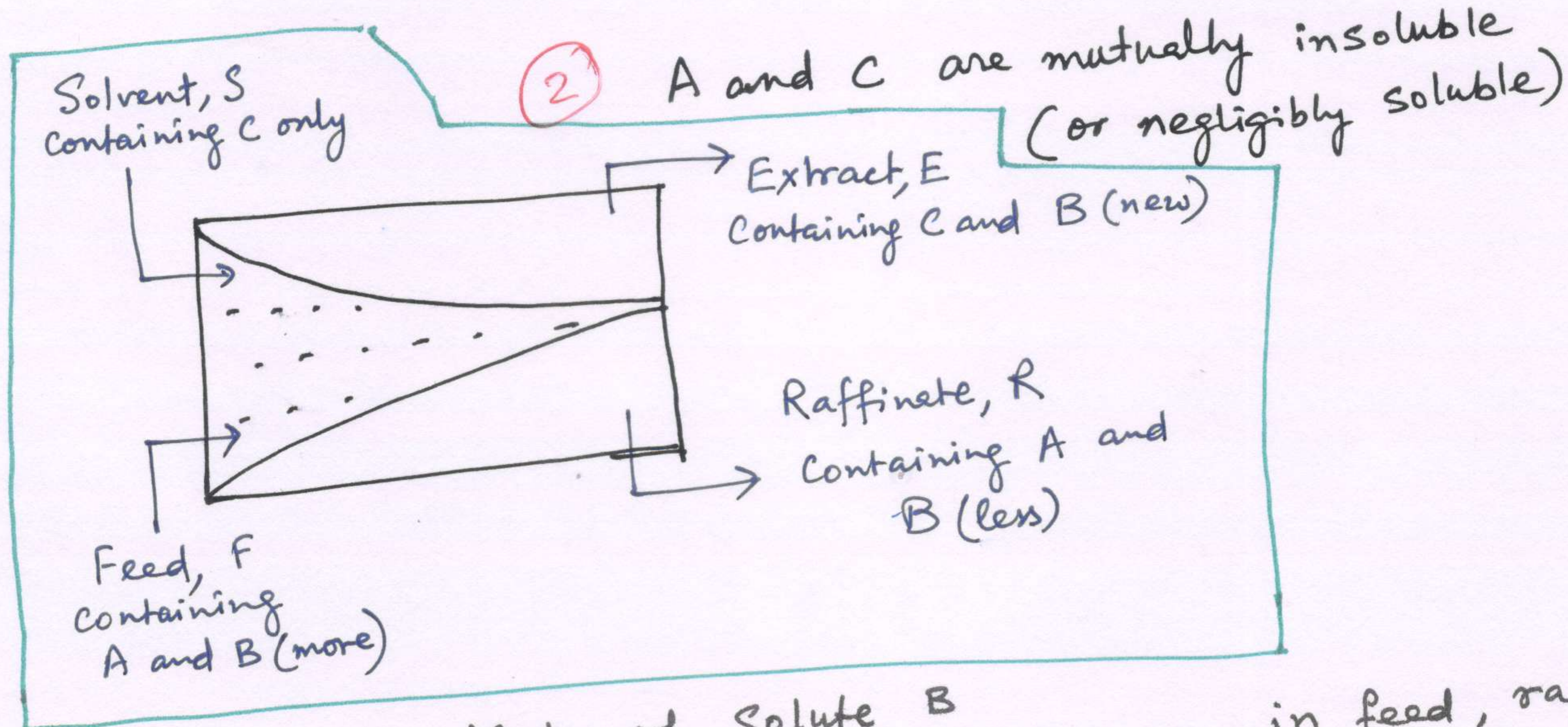


# Ternary liquid-liquid system.

(1)

Simplest case: (1) Only one solute component (B) that has appreciable solubility in Carrier (A) and Solvent (C)



$$X_B = \frac{\text{Moles of Solute B}}{\text{Moles of other component}}$$

in feed, raffinate, and extract as  $X_B^{(F)}$ ,  $X_B^{(R)}$ ,  $X_B^{(E)}$  respectively.

Total flow rate of feed is  $F$ .  
The feed rate of carrier A is  $F_A$ .

In another convention,

$X_B$  may be defined as the  $\frac{\text{mass of solute B}}{\text{mass of other component}}$  and the subsequent analysis would still be valid.

Solute material balance:

$$X_B^{(F)} F_A = X_B^{(E)} S + X_B^{(R)} F_A \quad \dots \text{Eq. 1}$$

At Equilibrium

$$\frac{X_B^{(E)}}{X_B^{(R)}} = K_{DB}'$$

= Distribution Coefficient  $\dots \text{Eq. 2}$

Combining Eq. 1 and Eq. 2

$$X_B^{(R)} = \frac{X_B^{(F)} F_A}{F_A + K_{DB}' S} = \frac{X_B^{(F)}}{1 + K_{DB}' \frac{S}{F_A}} = \frac{X_B^{(F)}}{1 + E_B}$$

$$\Rightarrow \frac{X_B^{(R)}}{X_B^{(F)}} = \text{Fraction of B that remains unextracted} = \frac{1}{1 + E_B} \quad \dots \text{Eq. 3}$$



## Simple Case of Ternary Liquid-Liquid System ... contd.

(2)

When extract and raffinate both are dilute in the solute, mass<sup>(or mole)</sup> fraction instead of mass<sup>(or mole)</sup> ratio can be used.

$$\left. \begin{array}{l} X = \text{Mass or mole ratio} \\ x = \text{Mass or mole fraction} \end{array} \right\} \begin{aligned} X_i &= \frac{x_i}{1-x_i} \\ \Rightarrow K_{D_i} &= \frac{x_i^{(1)} / (1-x_i^{(1)})}{x_i^{(2)} / (1-x_i^{(2)})} \\ &= K_{D_i} \left[ \frac{1-x_i^{(2)}}{1-x_i^{(1)}} \right] \end{aligned}$$

When  $x_i$  is small,  $K_{D_i}$  approaches  $K_D$

## Further interpretation of Distribution Coefficient

For each phase in a multiphase, multicomponent system, the total Gibbs Free energy is

$$G = G(T, P, N_1, N_2, \dots, N_i, \dots, N_c)$$

where  $N_i$  is number of moles of species 'i'.

At equilibrium, the total  $G$  for all phases is a minimum.

$\Rightarrow$  The total differential of  $G$  is zero.

The total differential of  $G$  is given by

$$dG = -SdT + VdP + \sum_{i=1}^c \mu_i dN_i$$

0  
for constant temperature

0  
for constant pressure

$\mu_i$  is the partial molar Gibbs free energy of species 'i', and is referred as chemical potential.

For  $N$  phases in equilibrium at uniform temperature and pressure, with each phase capable of mass transfer with another phase,

$$dG_{\text{system}} = \sum_{p=1}^N \left[ \sum_{i=1}^c \mu_i^{(p)} dN_i^{(p)} \right]_{P, T} \dots \dots \dots \text{Eq. 4}$$



# Simple case of Ternary Liquid-Liquid System - ... Contd.

(3)

Conservation of moles of each species across all phases in the system requires

$$\sum_{P=1}^N dN_i^{(P)} = 0 \Rightarrow dN_i^{(1)} + \sum_{P=2}^N dN_i^{(P)} = 0$$

$$\Rightarrow dN_i^{(1)} = - \sum_{P=2}^N dN_i^{(P)} \dots \dots \text{Eq. 5}$$

Following Eqn. 4 and Eqn. 5

$$dG_{\text{system}} = \sum_{i=1}^C \mu_i^{(1)} dN_i^{(1)} + \sum_{P=2}^N \left( \sum_{i=1}^C \mu_i^{(P)} dN_i^{(P)} \right)$$

$$= \sum_{i=1}^C \mu_i^{(1)} \left\{ - \sum_{P=2}^N dN_i^{(P)} \right\} + \sum_{P=2}^N \left( \sum_{i=1}^C \mu_i^{(P)} dN_i^{(P)} \right)$$

$$= \sum_{P=2}^N \left[ \sum_{i=1}^C \left\{ \mu_i^{(P)} - \mu_i^{(1)} \right\} dN_i^{(P)} \right]$$

Since  $dG_{\text{system}} = 0$  at equilibrium  $\Rightarrow \mu_i^{(P)} = \mu_i^{(1)}$

Each  $dN_i^{(P)}$  term can be varied independently of any other  $dN_i^{(P)}$  term.

This requires that each coefficient of  $dN_i^{(P)}$  is zero.

$$\Rightarrow \mu_i^{(P)} = \mu_i^{(1)} = \mu_i^{(2)} = \dots = \mu_i^{(N)}$$

Chemical potential is related to fugacity, and in turn to activity coefficient.

$$f_i = C e^{\mu_i / (RT)} \Rightarrow$$

$$\text{For liquid-liquid equilibria} \quad f_{iL}^{(1)} = f_{iL}^{(2)}$$

$$\text{Further } f_{iL} = \gamma_{iL} x_i f_{iL}^0$$

where  $\gamma_{iL}$  is the activity coefficient, and  $f_{iL}^0$  is fugacity of component 'i' as pure species at the same pressure and phase condition that remains same for each phase.

$$\Rightarrow \gamma_{iL}^{(1)} x_i^{(1)} f_{iL}^0 = \gamma_{iL}^{(2)} x_i^{(2)} f_{iL}^0$$

$$\Rightarrow \frac{x_i^{(1)}}{x_i^{(2)}} = \frac{\gamma_{iL}^{(2)}}{\gamma_{iL}^{(1)}} = K_{Di}$$

$$\Rightarrow K_{Di} = \frac{\gamma_{iL}^{(2)}}{\gamma_{iL}^{(1)}} = f(\text{equilibrium phase composition and temperature})$$



Thumb Rule: Choose a solvent that lowers the activity coefficient of the solute in comparison with the feed. Then  $K_D$  will be higher and  $x_B^{(E)}$  will be higher that is desired.

When the solute concentrations in extract and raffinate are small, the activity coefficients can be approximated by the values at infinite dilution.

$$\Rightarrow K_D = f(T) \text{ only}$$

In typical calculations, the extraction process can be considered isothermal, which allows use of constant  $K_D$

### Example Problem

Pure Solvent

$S = ?$

$$K_D = 0.657$$

in mass fraction which can be approximated as same for mass ratio.

Concentration of Solute B to be reduced to 1%.

Feed: 13,500 kg/h containing 8 wt. % solute (B) and rest carrier (A)

Solution

$$F_A = (1 - 0.08) 13,500 = 12,420 \text{ kg/h}$$

$$x_B^{(F)} = \frac{13,500 - 12,420}{12,420} = 0.087$$

Raffinate to contain 1 wt. % B

$$\Rightarrow x_B^{(R)} = \frac{0.01}{1 - 0.01} = 0.0101$$

Extraction Factor (As per Eqn. 3)

$$E_B = \frac{x_B^{(F)}}{x_B^{(R)}} - 1 = \frac{0.087}{0.0101} - 1 = 7.61$$

Further  $E_B = \frac{S K_D'}{F_A}$

$$\Rightarrow S = \frac{E_B F_A}{K_D'} = \frac{7.61 \times 12,420}{0.657} = 1,44,000 \text{ kg/h}$$

Feed Stream: 13,500 kg/h

Solvent Stream (Required): 1,44,000 kg/h

Feasibility?



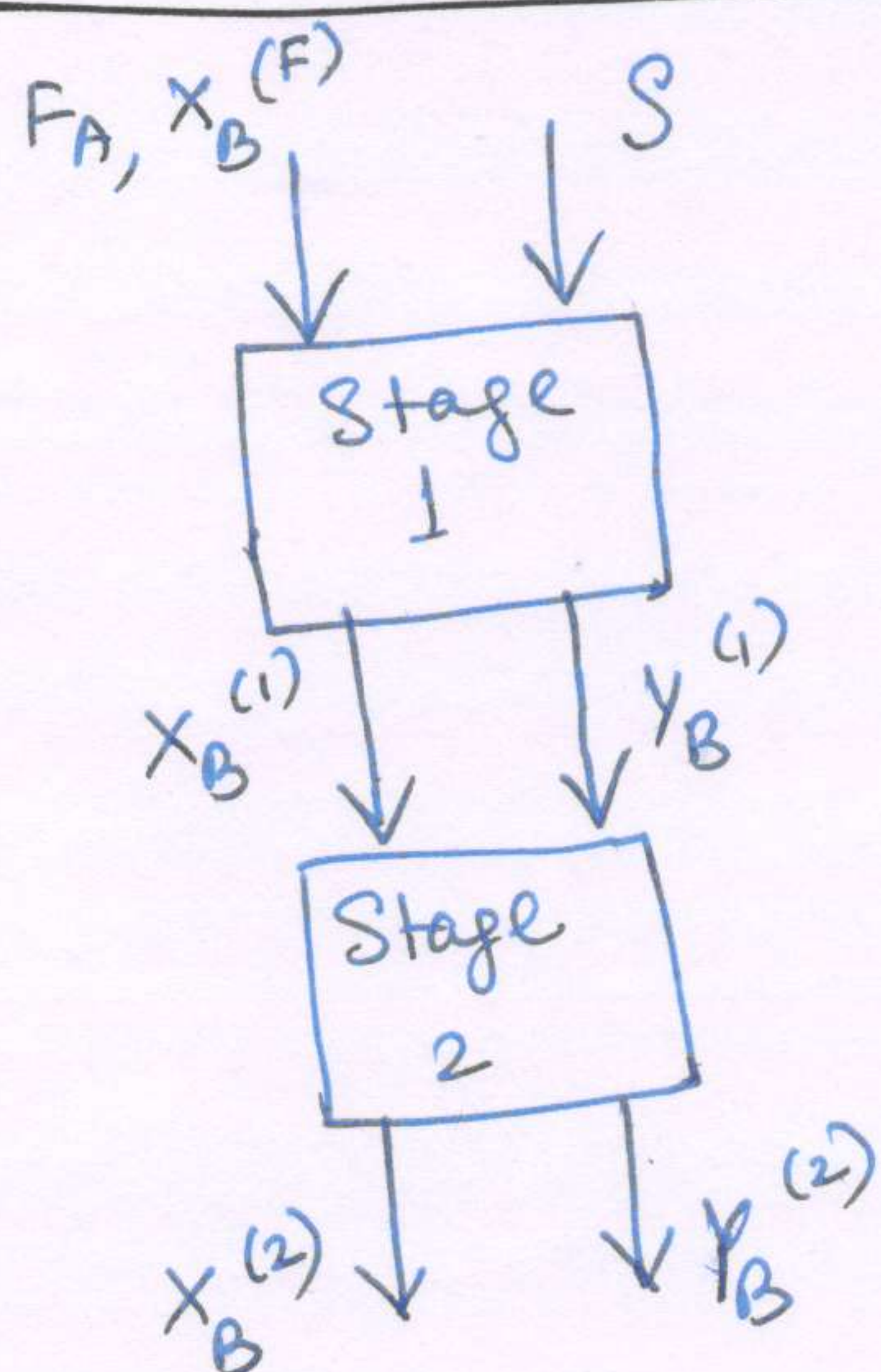
# Simple Liquid-Liquid Extraction . . . . contd.

(5)

Separation Cascade: A collection of contacting stages

Extract stream Mass Ratio is referred as  $Y_B$ , since the superscript will now be used to mark the Stage Number.

Co-current Cascade



At the end of 1<sup>st</sup> stage, material balance for B gives

$$X_B^{(F)} F_A + 0 = X_B^{(1)} F_A + Y_B^{(1)} S \quad \dots \text{Eq. 6}$$

$$= X_B^{(1)} F_A + K_{DB}' X_B^{(1)} S$$

$$= X_B^{(1)} [F_A + K_{DB}' S]$$

$$\Rightarrow \frac{Y_B^{(1)}}{X_B^{(F)}} = \frac{K_{DB}'}{1+E}$$

For the second stage, material balance for B gives

$$X_B^{(1)} F_A + Y_B^{(1)} S = X_B^{(2)} F_A + Y_B^{(2)} S$$

$$\text{and } K_{DB}' = \frac{Y_B^{(2)}}{X_B^{(2)}} \Rightarrow$$

$$\begin{aligned} &= X_B^{(2)} F_A + K_{DB}' X_B^{(2)} S \\ &= X_B^{(2)} [F_A + K_{DB}' S] \end{aligned}$$

From Eqn. 6,

$$\text{L.H.S.} = X_B^{(F)} F_A$$

Equating L.H.S. with R.H.S.

$$\frac{X_B^{(2)}}{X_B^{(F)}} = \frac{1}{1+E} = \frac{X_B^{(N)}}{X_B^{(F)}} \quad \text{By induction after N stages.}$$

$$\Rightarrow X_B^{(2)} = X_B^{(1)}$$

(No additional extraction due to addition of second stage).

Note the superscript

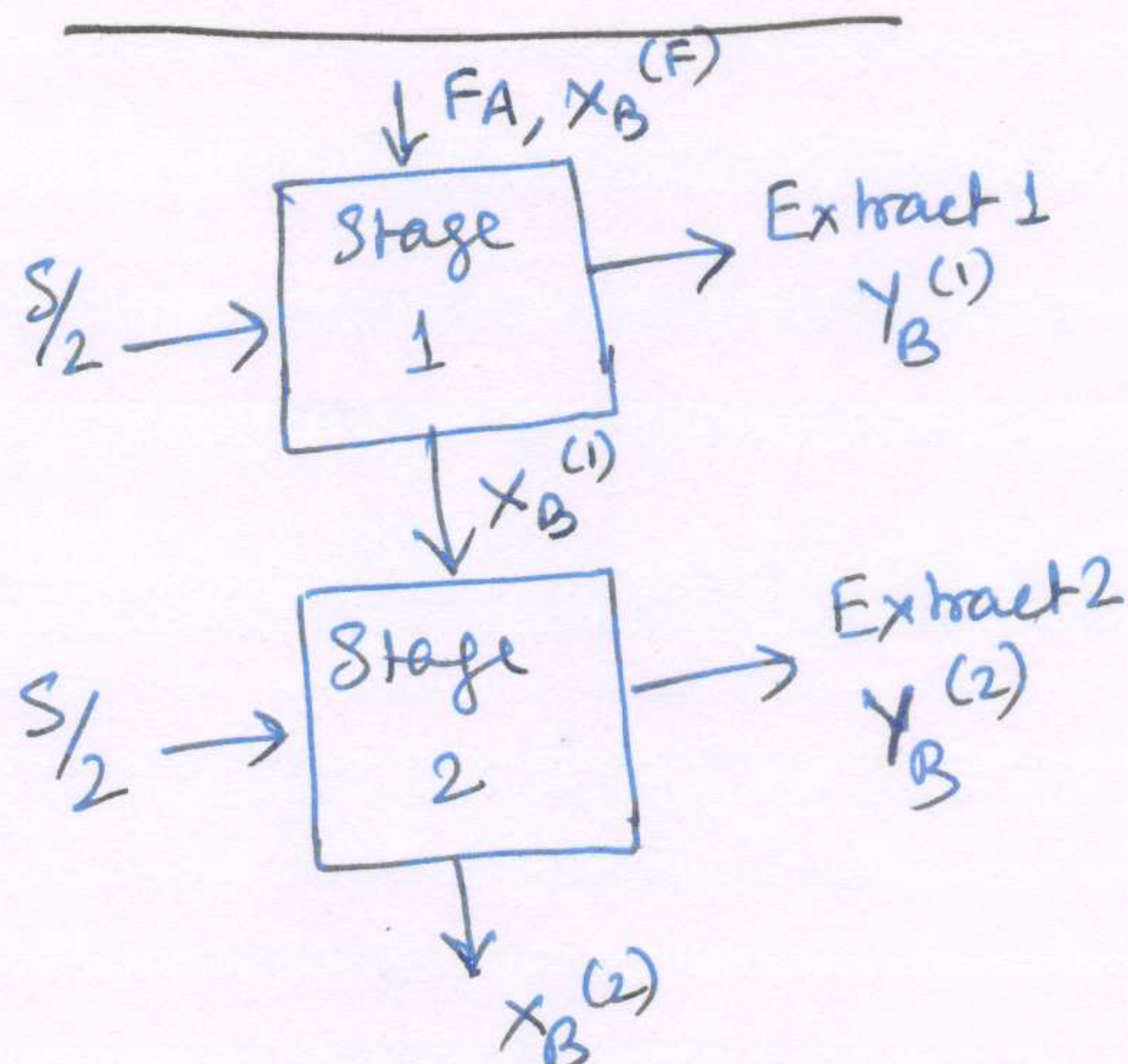
the stream leaving a stage bears the stage no. as superscript.



# Simple Liquid-Liquid Extraction . . . . . contd.

(6)

## Cross-current cascade



First stage can be treated as isolated single stage

$$\frac{X_B^{(1)}}{X_B^{(F)}} = \frac{1}{1 + \frac{K_{DB}'(S/2)}{F_A}} = \frac{1}{1 + E/2}$$

Similarly,

$$\frac{X_B^{(2)}}{X_B^{(1)}} = \frac{1}{1 + E/2}$$

For N stages

$$\frac{X_B^{(N)}}{X_B^{(F)}} = \frac{X_B^{(N)}}{X_B^{(N-1)}} \cdot \frac{X_B^{(N-1)}}{X_B^{(N-2)}} \cdots \frac{X_B^{(1)}}{X_B^{(F)}} = \frac{1}{\left(1 + \frac{E}{N}\right)^N}$$

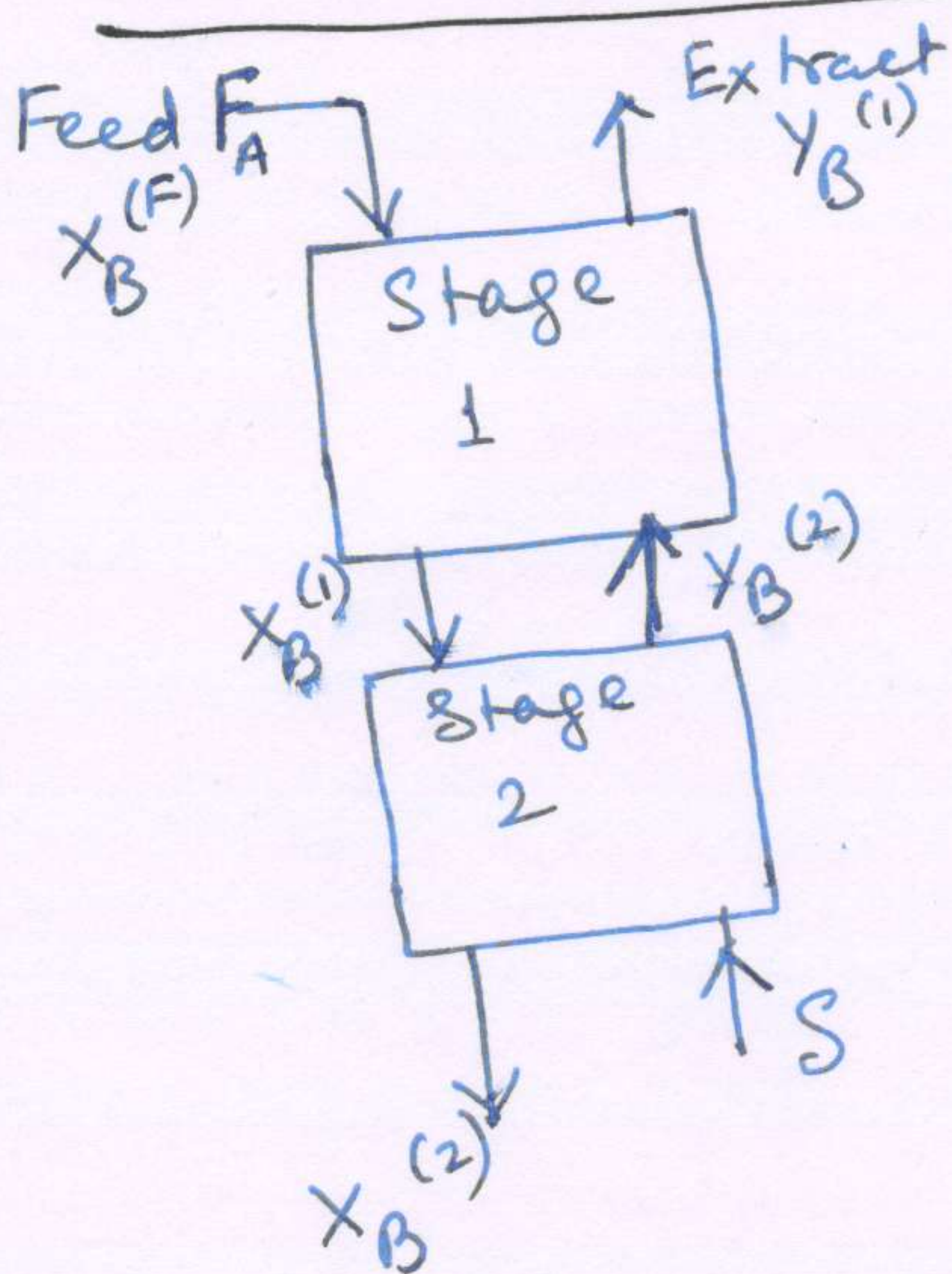
$$\frac{X_B^{(N)}}{X_B^{(N-1)}} = \frac{1}{1 + E/N}$$

assuming  $S/N$  as the solvent mass flow rate to each stage

$$\lim_{N \rightarrow \infty} \frac{X_B^{(N)}}{X_B^{(F)}} = \frac{1}{e^E} > 0$$

(complete extraction not possible)

## Counter current cascade



For Stage 1

$$X_B^{(F)} F_A + Y_B^{(2)} S = X_B^{(1)} F_A + Y_B^{(1)} S$$

and  $K_{DB}' = \frac{Y_B^{(1)}}{X_B^{(1)}}$

For Stage 2

$$X_B^{(1)} F_A = X_B^{(2)} F_A + Y_B^{(2)} S$$

and  $K_{DB}' = \frac{Y_B^{(2)}}{X_B^{(2)}}$

$$\Rightarrow X_B^{(1)} = X_B^{(2)} \left[ \frac{F_A + K_{DB}' S}{F_A} \right]$$

$$X_B^{(F)} F_A + K_{DB}' X_B^{(2)} S = X_B^{(2)} \left[ \frac{F_A + K_{DB}' S}{F_A} \right] F_A + K_{DB}' X_B^{(2)} \left[ \frac{F_A + K_{DB}' S}{F_A} \right] S$$

For N-Counter current stages

$$\frac{X_B^{(N)}}{X_B^{(F)}} = \frac{1}{\sum_{n=0}^N E^n}$$

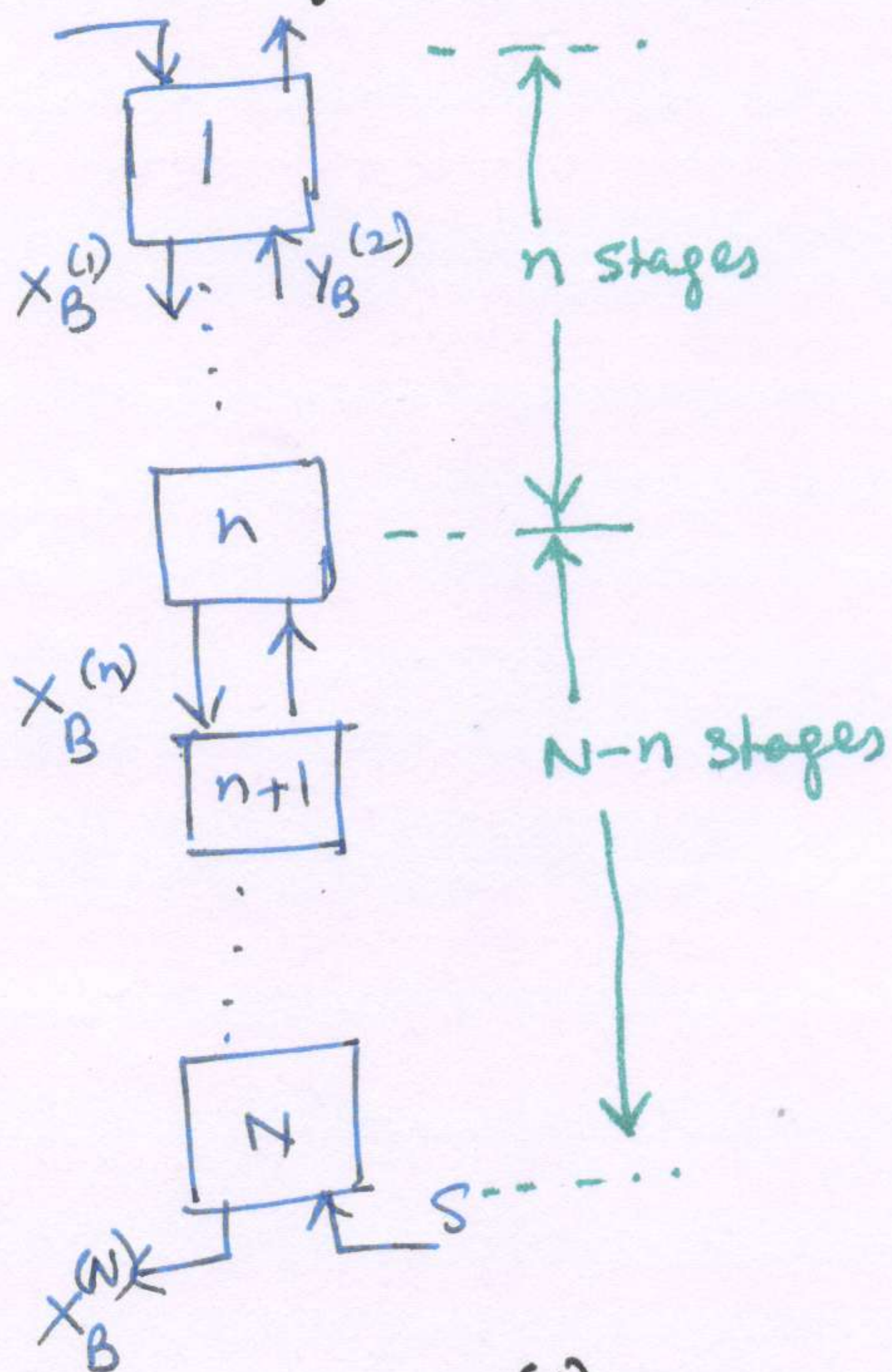
$$\Rightarrow \frac{X_B^{(2)}}{X_B^{(F)}} = \frac{1}{1 + E + E^2}$$

where  $E = \frac{K_{DB}' S}{F_A}$



# Simple liquid-liquid Extraction - . . . contd.

Interstage values of  $x_B$  in counter current cascade



$$\frac{x_B^{(N)}}{x_B^{(n)}} = \frac{1}{\sum_{k=0}^{N-n} E^k}$$

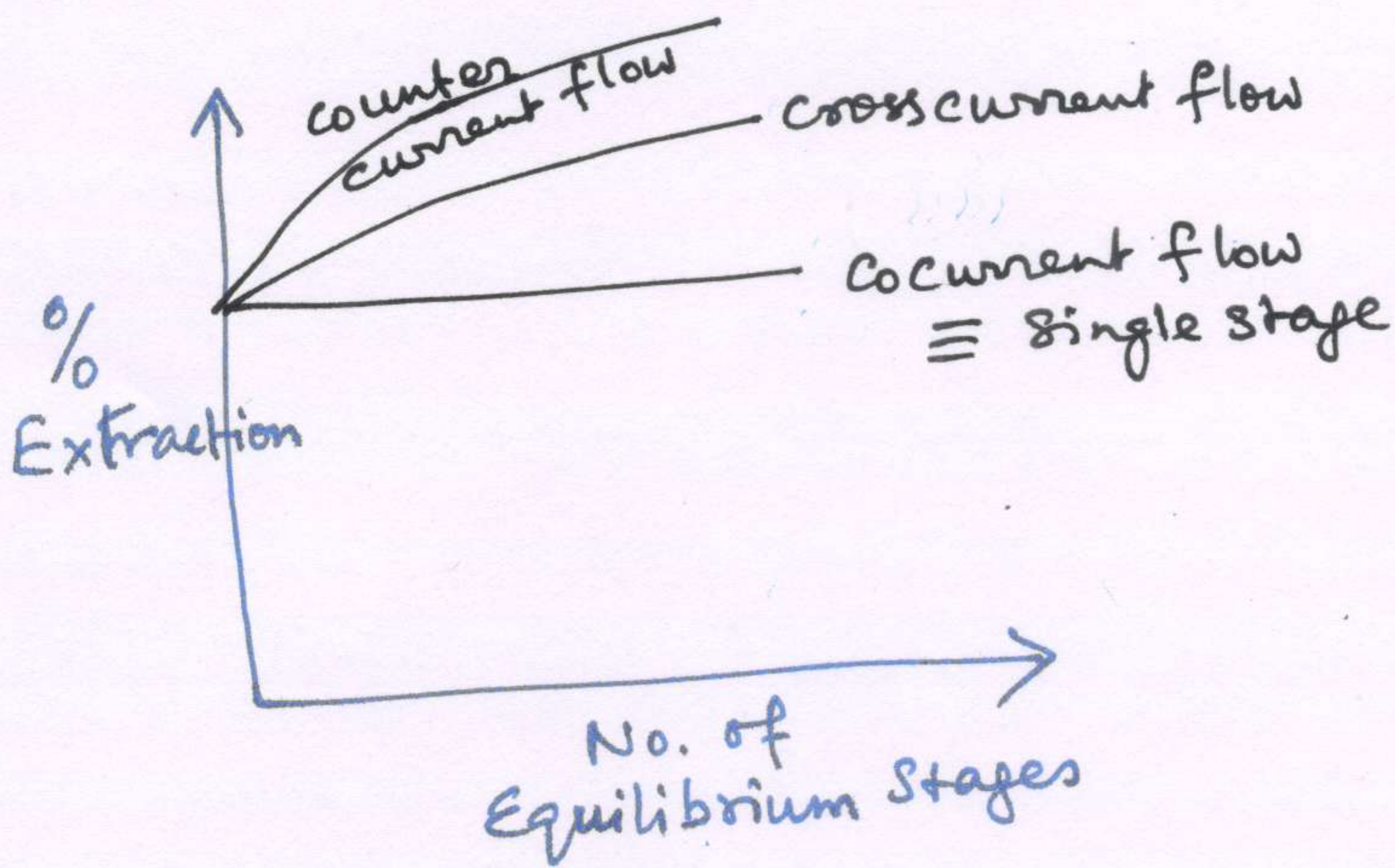
$$\frac{x_B^{(N)}}{x_B^{(F)}} = \frac{1}{\sum_{k=0}^N E^k}$$

$$\Rightarrow \frac{x_B^{(n)}}{x_B^{(F)}} = \frac{\sum_{k=0}^{N-n} E^k}{\sum_{k=0}^N E^k}$$

$$\lim_{N \rightarrow \infty} \frac{x_B^{(N)}}{x_B^{(F)}} = 1 - E \quad \text{for } E \leq 1$$

$$= 0 \quad \text{for } 1 < E \leq \infty$$

Complete extraction can be achieved when  $E > 1$



Counter current extraction is most efficient.

(\*) Repeat the single-stage problem with two-stages, calculate S.