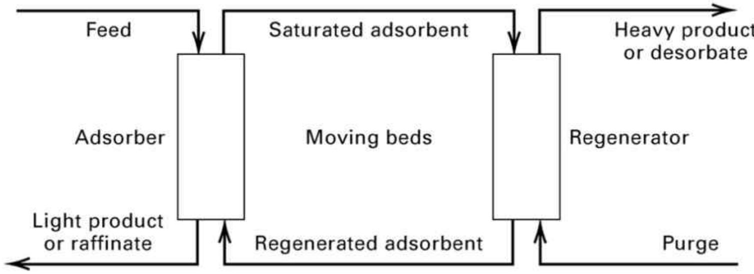
Lecture 9.
Continuous Adsorption Systems

- McCabe-Thiele Method for Purification
- Kremser Method
- McCabe-Thiele Method for Bulk Separation
- Simulated-Moving-Bed Systems
- Models for SMB Systems
  - TMB equilibrium-stage model using a McCabe-Thiele-type analysis
  - Steady-state local-adsorption-equilibrium TMB model
  - Steady-state TMB model
  - Dynamic SMB model

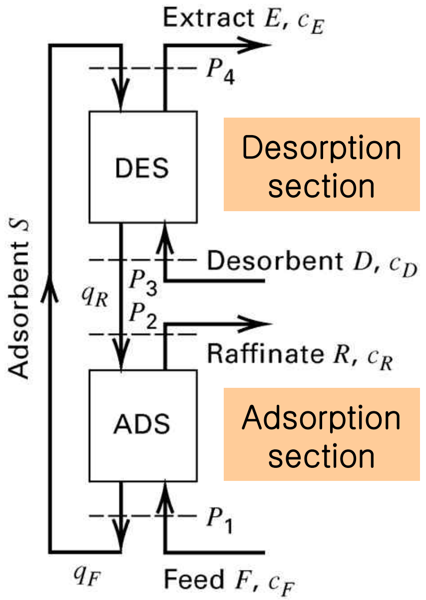
Continuous, Countercurrent Operation

- Advantage of continuous, countercurrent operation

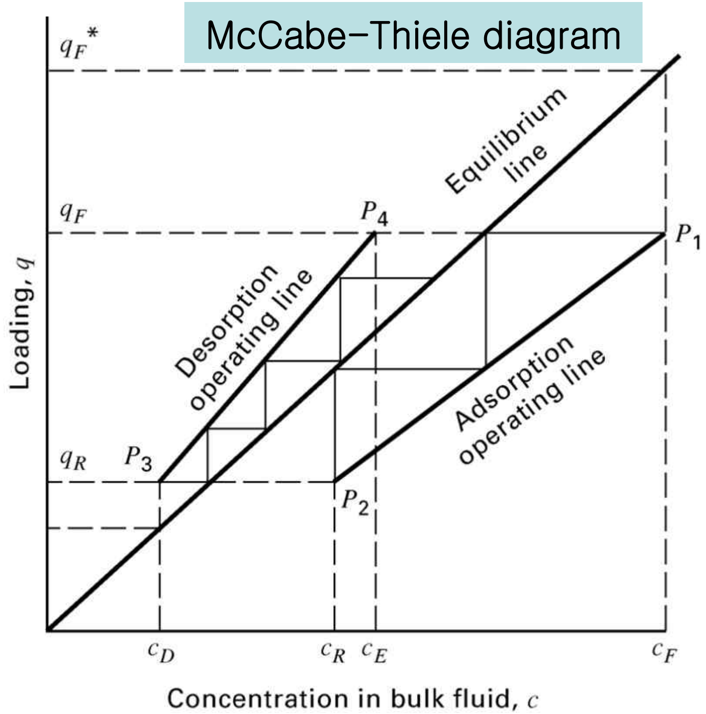
  : countercurrent flow maximizes the average driving force for transport → increases adsorbent use efficiency



- McCabe–Thiele and Kremser methods for purification



- If the system is dilute in solute, and solute adsorption isotherms for feed solvent and purge fluid are identical
- The operating and equilibrium lines are straight because of the dilute condition



McCabe–Thiele Method for Purification

- Position of operating lines based on direction for mass transfer
  - Adsorption operating line lies below the equilibrium line
  - Desorption operating line lies above the equilibrium line

- Adsorption operating line

$$q = \frac{F}{S}(c - c_F) + q_F$$

- Desorption operating line

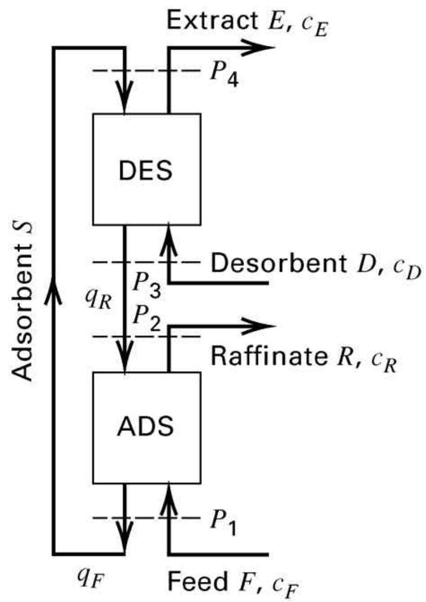
$$q = \frac{D}{S}(c - c_D) + q_R$$

- Equilibrium line

$$q = Kc$$

F, S, and D are solute–free mass flow rates

All solute concentrations are per solute–free carrier

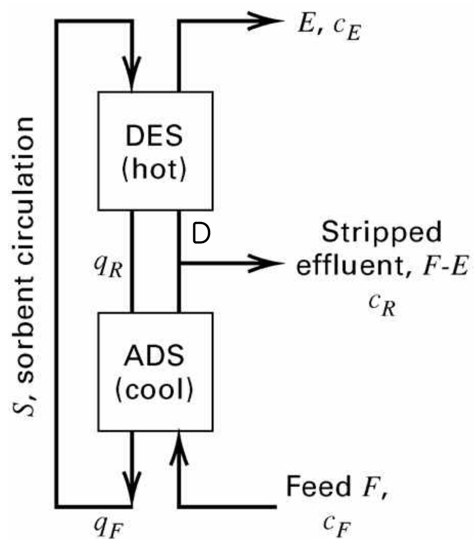


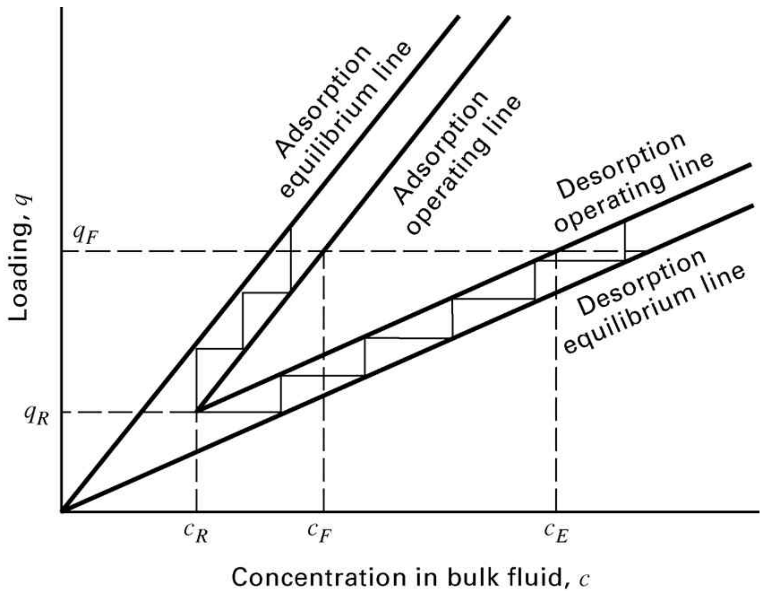
- When c_D and c_R approach zero, in order to avoid a large number of stages:

$$\frac{F}{S} < K < \frac{D}{S}$$

McCabe–Thiele Method for Desorption at Elevated Temperature

- If the temperature or pressure for the two sections can be altered to place the equilibrium line for desorption below that for adsorption → it becomes possible to use a portion of the raffinate for desorption
  - F/S can be greater than D/S
  - With a portion of raffinate used in Bed 2 (DES), the net raffinate product is F−D
  - The two operating lines must intersect at the point (q_R, c_R)
  - By adjusting D/F, intersect point can be moved closer to the origin to increase raffinate purity, c_R, but at the expense of more stages and deeper beds





Kremser Method

- When the equilibrium and operating lines are straight

$$N_t = \frac{\ln\left[\dfrac{c_1 - q_1/K}{c_2 - q_2/K}\right]}{\ln\left[\dfrac{c_1 - c_2}{q_1/K - q_2/K}\right]}$$

1 and 2 refer to opposite ends which are chosen so $q_1 > q_2$

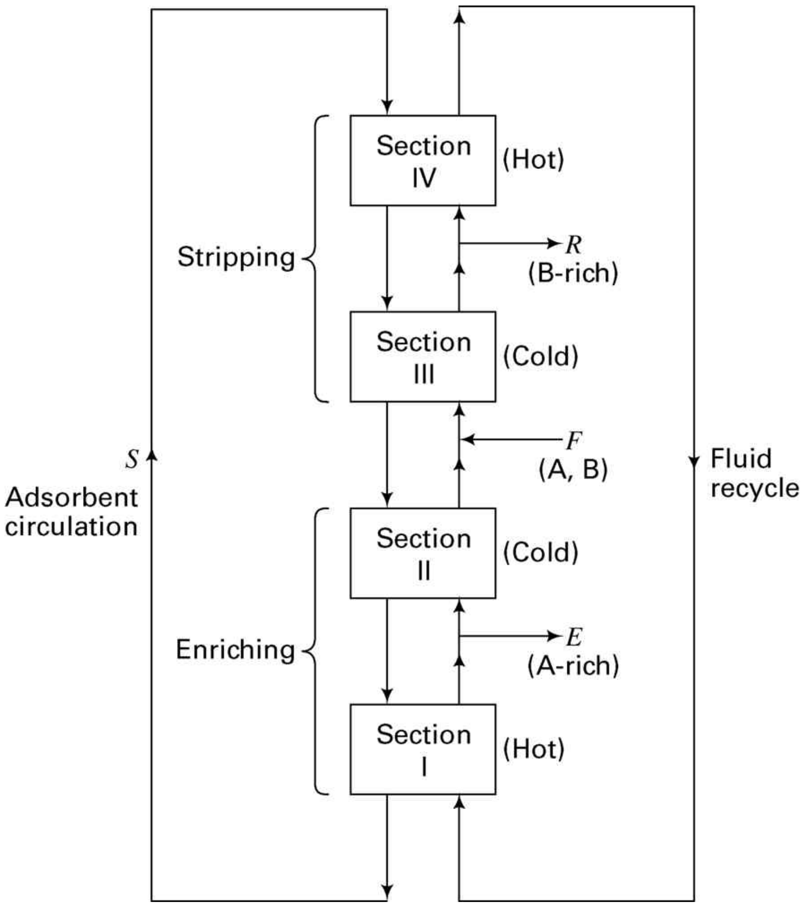
- For a number of theoretical stages, N_t, in the adsorption or desorption sections

Bed height $L = N_t(\mathrm{HETP})$

  - Values of HETP, which depend on mass-transfer resistances and axial dispersion, must be established from experimental measurements
  - For large-diameter beds, values of HETP are in the range of 0.5-1.5 ft

McCabe–Thiele Method for Bulk Separation

- Continuous, countercurrent bulk separation for binary mixture

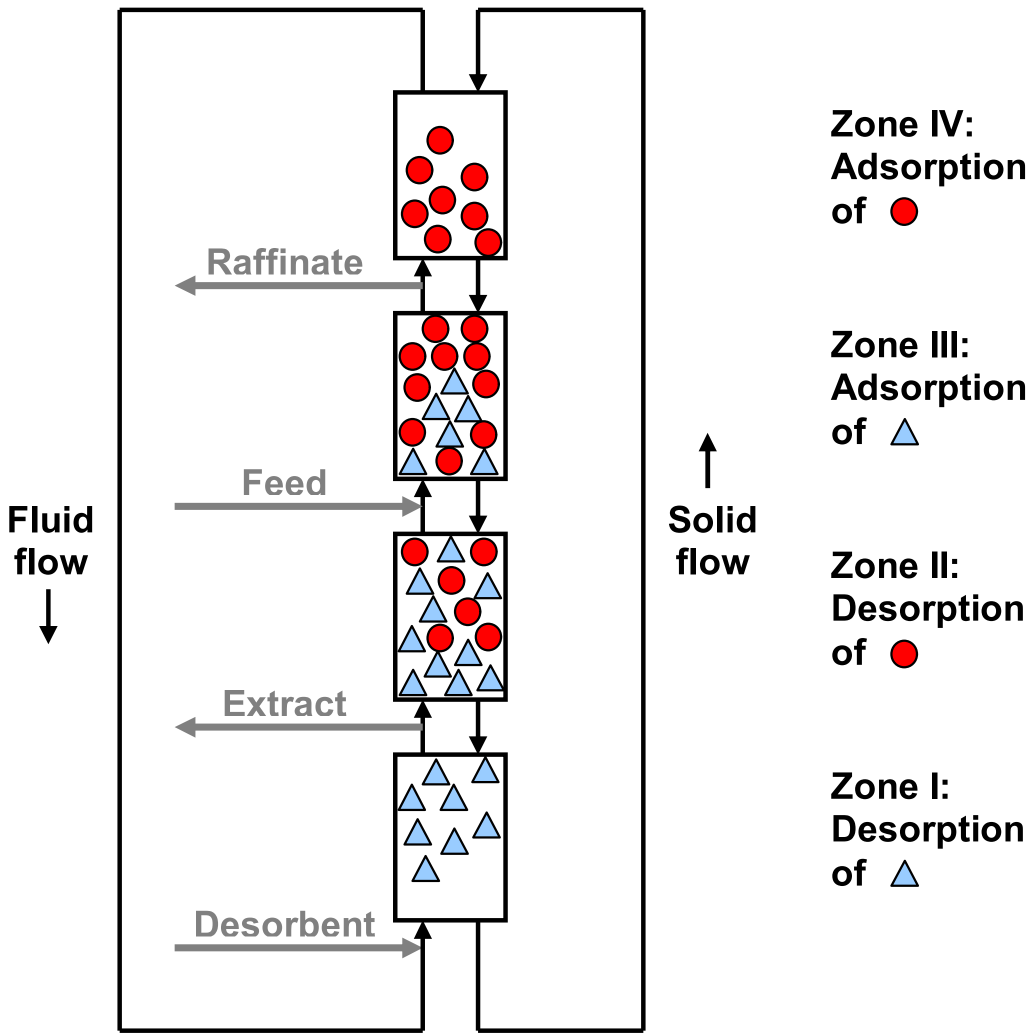


Component A is more strongly adsorbed than B

- To provide flexibility, a thermal swing is used, with Sections II and III operating at low or ambient temperature, while Sections I and IV operate at elevated temperature
- The top two sections (III and IV) provide a stripping action to produce a product rich in the less strongly adsorbed component B
- The two bottom sections (I and II) provide an enriching action to produce a product rich in component A

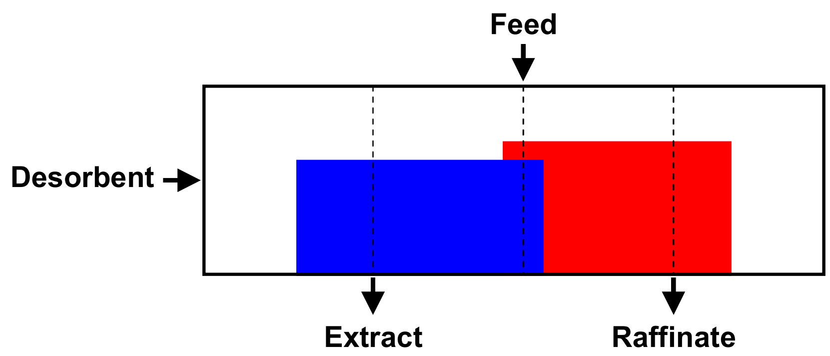
Simulated-Moving-Bed Systems (1)

- True-moving bed



- Steady state after the start-up
- Time independent model

- Concept of a SMB system



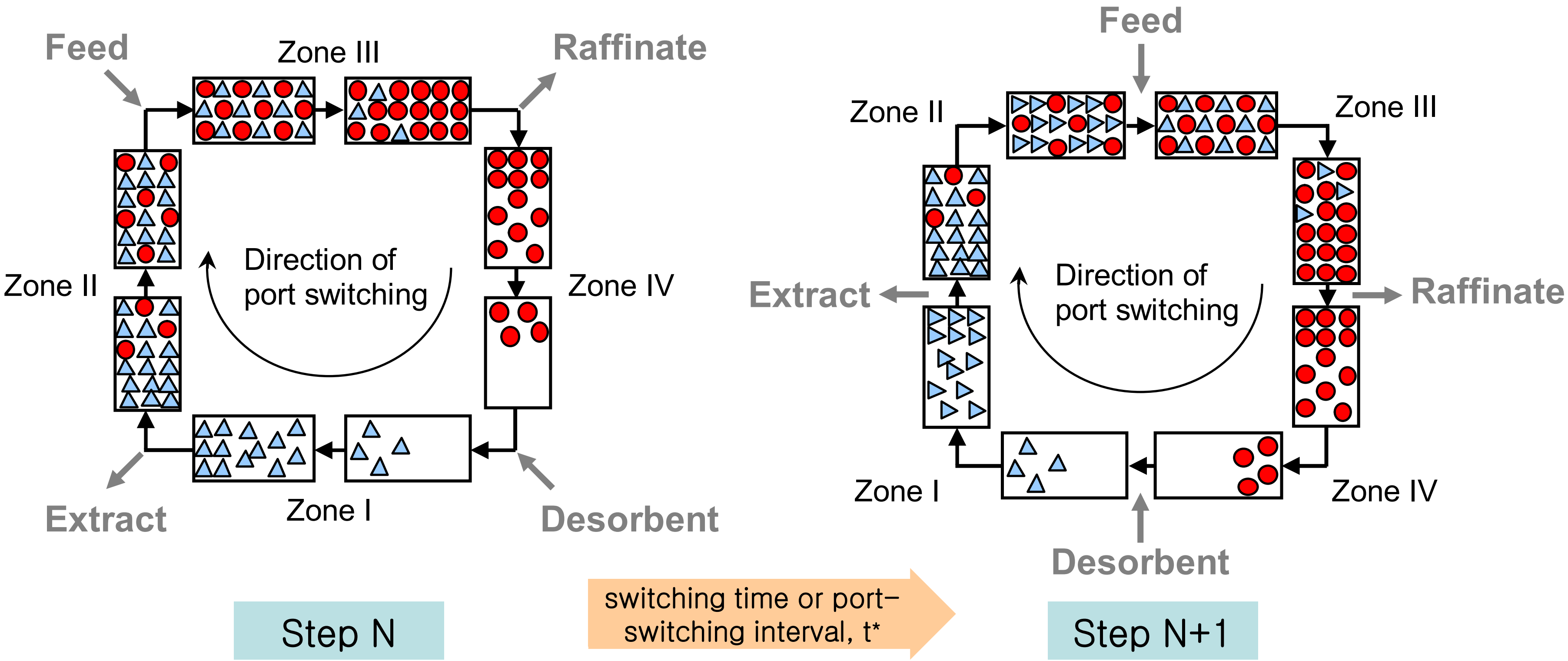
Simulated-Moving-Bed Systems (2)

- Difficulties in operating continuous, countercurrent moving-bed (true-moving-bed, TMB) systems: adsorbent abrasion, failure to achieve particle plug flow, fluid channeling
- Continuous, countercurrent operation can be simulated by using a column containing a series of fixed beds and periodically moving the locations at which streams enter and leave the column : simulated moving-bed (SMB) systems
  - Widespread commercial application for liquid separations in the petrochemical, food, biochemical, pharmaceutical, and fine chemical industries
  - An SMB can be treated as a countercurrent cascade of sections (or zones) rather than stages, where stream entry or withdrawal points bound the sections
  - As each section is divided into more subsections, the SMB system more closely approaches the separation achieved in a corresponding TMB

Simulated-Moving-Bed Systems (3)

- Operation of SMB

- Cyclic steady state
- Time dependent model



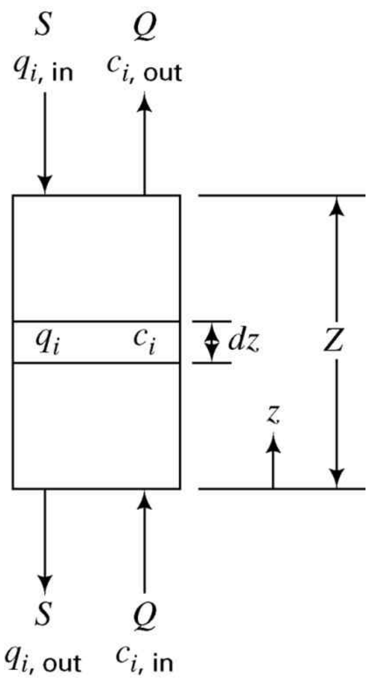
- By periodically shifting feed and product positions by one port position in the direction of fluid flow, movement of solid adsorbent in the opposite direction is simulated
- Flow rates in the four sections are different

Models for SMB Systems

- Models for designing and analyzing SMBs
  - Models assuming steady-state conditions with continuous, countercurrent flows of fluid and solid adsorbent, approximating SMB operation with a TMB
    - TMB equilibrium-stage models using a McCabe-Thiele-type analysis
      : simplest, but difficult to apply to systems with nonlinear adsorption-equilibrium isotherms
    - TMB local-adsorption-equilibrium models
      : ignoring effects of axial dispersion and fluid-particle mass transfer; useful for establishing reasonable operating flow rates in multiple sections of an SMB (∵ for many applications, behavior of an SMB is determined largely by adsorption equilibria)
    - TMB rate-based models
      : account for axial dispersion in the bed, particle-fluid mass-transfer resistances, and nonlinear adsorption isotherms; preferred for a final design
  - SMB rate-based models: apply to transient operation for startup, approach to cyclic steady state, and shutdown

Steady-State Local-Adsorption-Equilibrium TMB Model (1)

- TMB local-adsorption-equilibrium model for a single section



- Assumptions
  - One-dimensional plug flow of both phases with no channeling
  - Constant volumetric flow rates (Q for liquid and Q_s for solid)
  - Constant external void fraction, ε_b, of solids bed
  - Negligible axial dispersion and particle-fluid mass-transfer resistances
  - Local adsorption equilibrium between solute concentrations, c_i, in the bulk liquid and adsorption loading, q_i, on the solid
  - Isothermal and isochoric conditions

- Mass balance

$$Q\frac{dc_i}{dz} - S\frac{dq_i}{dz} = 0$$

- Boundary conditions

$$z = 0, c_i = c_{i,\text{in}} \text{ and } z = Z, q_i = q_{i,\text{in}}$$

Steady-State Local-Adsorption-Equilibrium TMB Model (2)

- Usefulness of local-equilibrium theory

  : approximate determinations of the amount of solid adsorbent and fluid flow rates, in each TMB section, to achieve a perfect separation of two solutes
- Assuming adsorption equilibrium is linear for a dilute feed, with $K_A > K_B$
- Flow rate ratios for each section j

$$m_j = \frac{Q_j}{Q_s} = \frac{\text{volumetric fluid phase flow rate}}{\text{volumetric solid particle phase flow rate}}$$

- For local adsorption equilibrium, the necessary and sufficient conditions at each section for complete separation

$K_A < m_I < \infty$	Ensures that net flow rates of components A and B will be positive (upward) in Section I
$0 < m_{IV} < K_B$	Ensures that net flow rates of components A and B will be negative (downward) in Section IV

Steady-State Local-Adsorption-Equilibrium TMB Model (3)

$$K_{\mathrm{B}} < m_{\mathrm{II}} < K_{\mathrm{A}}$$

$$K_{\mathrm{B}} < m_{\mathrm{III}} < K_{\mathrm{A}}$$

Ensure sharpness of the separation by causing net flow rates of A and B to be negative (downward) and positive (upward), respectively, in the two central Sections II and III

- Inequality constraints can be converted to equality constraints using the safety margin, β

$$\begin{cases} Q_{\mathrm{I}}/Q_{\mathrm{S}} = K_{\mathrm{A}}\beta \\ (Q_{\mathrm{I}} - Q_{\mathrm{E}})/Q_{\mathrm{S}} = K_{\mathrm{B}}\beta \\ (Q_{\mathrm{I}} - Q_{\mathrm{E}} + Q_{\mathrm{F}})/Q_{\mathrm{S}} = K_{\mathrm{A}}/\beta \\ (Q_{\mathrm{I}} - Q_{\mathrm{E}} + Q_{\mathrm{F}} - Q_{\mathrm{R}})/Q_{\mathrm{S}} = K_{\mathrm{B}}/\beta \end{cases} \xrightarrow{\text{eliminating } Q_{\mathrm{I}}} \begin{aligned} Q_{\mathrm{S}} &= \frac{Q_{\mathrm{F}}}{K_{\mathrm{A}}/\beta - K_{\mathrm{B}}\beta} \\ Q_{\mathrm{E}} &= Q_{\mathrm{S}}(K_{\mathrm{A}} - K_{\mathrm{B}})\beta \\ Q_{\mathrm{R}} &= Q_{\mathrm{S}}(K_{\mathrm{A}} - K_{\mathrm{B}})/\beta \end{aligned}$$

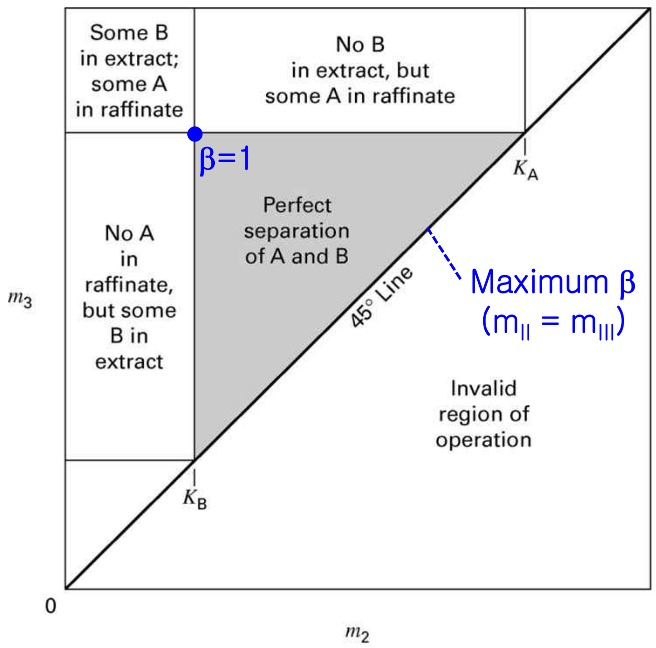
$$Q_{\mathrm{I}} = Q_{\mathrm{C}} + Q_{\mathrm{D}} = Q_{\mathrm{S}}K_{\mathrm{A}}\beta \Rightarrow Q_{\mathrm{C}} = Q_{\mathrm{S}}K_{\mathrm{A}}\beta - Q_{\mathrm{D}}$$

Q_{C} : fluid recirculation rate before adding makeup desorbent

- By an overall material balance, $Q_{\mathrm{D}} = Q_{\mathrm{E}} + Q_{\mathrm{R}} - Q_{\mathrm{F}}$

Steady–State Local–Adsorption–Equilibrium TMB Model (4)

- Triangle method



  - If values m_{II} and m_{III} within the triangular region are selected, a perfect separation is possible
  - If $m_{II} < K_B$, some B appears in extract
  - If $m_{III} > K_A$, some A appears in raffinate
  - If $m_{II} < K_B$ and $m_{III} > K_A$, extract contains some B and raffinate contains some A

- Safety margin, $1 \leq \beta \leq \sqrt{K_A / K_B}$
  - Above a maximum β, some sections will encounter negative fluid flow rates, and when β < 1, perfect separation will not be achieved
  - As the value of β increases from minimum to maximum, fluid flow rates in the sections increase, often exponentially
  - As separation factor $K_A/K_B \to 1$, permission range of β becomes smaller

Steady-State TMB Model (1)

- Unlike the local-adsorption-equilibrium model, axial dispersion and fluid-particle mass transfer are considered
- Mass-balance equation for the bulk fluid phase, f

$$-D_{L_j}\frac{d^2 c_{i,j}}{dz^2}+u_{f_j}\frac{dc_{i,j}}{dz}+\frac{(1-\varepsilon_b)}{\varepsilon_b}J_{i,j}=0$$

J_i : mass-transfer flux between the bulk fluid phase and the sorbate in the pores
u_f : interstitial fluid velocity $u_{f_j}=Q_j/\varepsilon_b A_b$

- Mass-balance for sorbate, s, on the solid phase

$$u_s\frac{d\bar{q}_{i,j}}{dz}-J_{i,j}=0$$

u_s : true moving-solid velocity $u_s=\dfrac{Q_S}{(1-\varepsilon_b)A_b}$

- Fluid-to-solid mass transfer

$$J_{i,j}=k_{i,j}\left(q^*_{i,j}-\bar{q}_{i,j}\right)$$

- Adsorption isotherm $q^*_{i,j}=f\{\text{all}\, c_{i,j}\}$

Steady-State TMB Model (2)

- Boundary conditions
  - At the section entrance, z=0 (accounting for axial dispersion)

$$u_{f_j}(c_{i,j,0} - c_{i,j}) = -\varepsilon_b D_{L_j} \frac{dc_{i,j}}{dz}$$

  - At Sections I and II where extract is withdrawn

$$c_{i,\mathrm{I},z=L_j} = c_{i,\mathrm{II},z=0} \qquad q_{i,\mathrm{I},z=L_j} = q_{i,\mathrm{II},z=0}$$

  - At Sections III and IV where raffinate is withdrawn

$$c_{i,\mathrm{III},z=L_j} = c_{i,\mathrm{IV},z=0} \qquad q_{i,\mathrm{III},z=L_j} = q_{i,\mathrm{IV},z=0}$$

  - At Sections II and III where feed enters

$$c_{i,\mathrm{III},z=0} = \left(Q_{\mathrm{II}}/Q_{\mathrm{III}}\right)c_{i,\mathrm{II},z=L_j} + \left(Q_{\mathrm{F}}/Q_{\mathrm{III}}\right)c_{i,F} \qquad q_{i,\mathrm{II},z=L_j} = q_{i,\mathrm{III},z=0}$$

  - At Sections IV and I where make-up desorbent enters

$$c_{i,\mathrm{I},z=0} = \left(Q_{\mathrm{IV}}/Q_{\mathrm{I}}\right)c_{i,\mathrm{IV},z=L_j} + \left(Q_{\mathrm{D}}/Q_{\mathrm{I}}\right)c_{i,D} \qquad q_{i,\mathrm{IV},z=L_j} = q_{i,\mathrm{I},z=0}$$

Steady-State TMB Model (3)

- Volumetric fluid flow rates

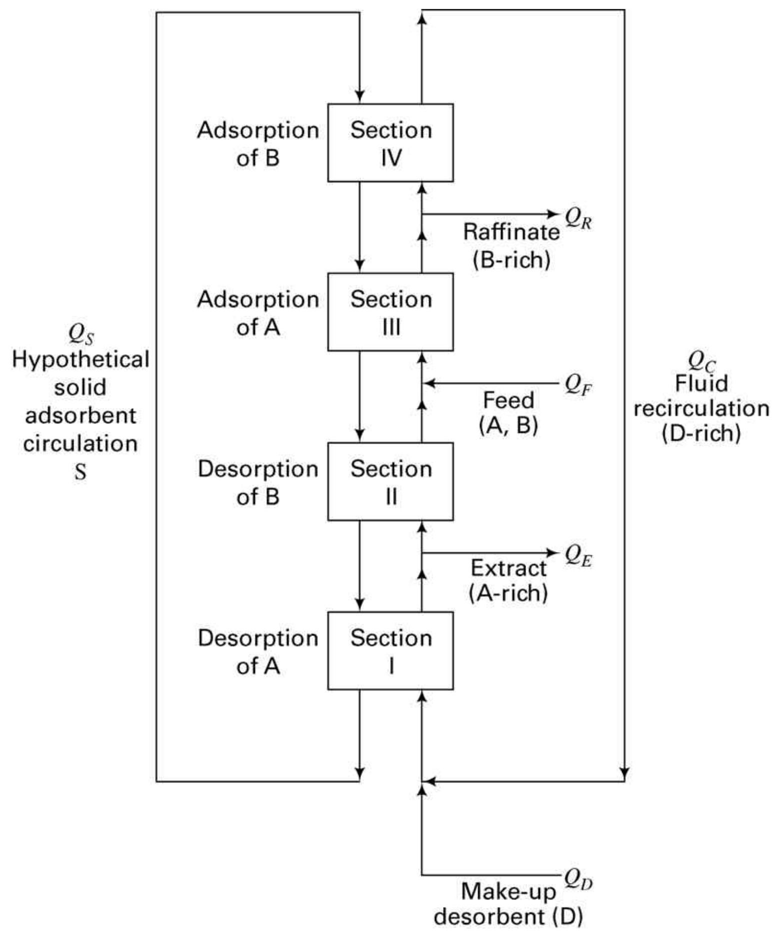
$$Q_{\mathrm{I}} = Q_{\mathrm{IV}} + Q_D$$

$$Q_{\mathrm{II}} = Q_{\mathrm{I}} - Q_E$$

$$Q_{\mathrm{III}} = Q_{\mathrm{II}} + Q_F$$

$$Q_{\mathrm{IV}} = Q_{\mathrm{III}} - Q_R$$

- To obtain the same true velocity difference between fluid and solid particles, upward fluid velocity in the SMB must be the sum of the absolute true velocities in the upward-moving fluid and the downward-moving solid particles in the TMB



$$(Q_j)_{\mathrm{SMB}} = (Q_j)_{\mathrm{TMB}} + \left(\frac{\varepsilon_b}{1-\varepsilon_b}\right)(Q_S)_{\mathrm{TMB}}$$

Dynamic SMB Model

- Equations take into account time of operation, t, use a fluid velocity relative to the stationary solid particles, and must be written for each bed subsection, k, between adjacent ports
- Mass-balance equation for the bulk fluid phase, f

$$\frac{\partial c_{i,k}}{\partial t} - D_{L_j}\frac{\partial^2 c_{i,k}}{\partial z^2} + u_{f_k}\frac{\partial c_{i,k}}{\partial z} + \frac{(1-\varepsilon_b)}{\varepsilon_b}J_{i,k} = 0$$

- Mass-balance for sorbate on the solid phase

$$\frac{\partial \bar{q}_{i,k}}{\partial t} - J_{i,k} = 0$$

Interstitial fluid velocity $(u_f)_{\mathrm{SMB}} = (u_f)_{\mathrm{TMB}} + \left|(u_s)\right|_{\mathrm{TMB}}$

$$u_s = L_k / t^*$$

L_k : bed height between adjacent ports
t^* : port-switching time

- Boundary conditions for TMB models apply to SMB models. In addition, initial conditions are needed for $c_{i,j}$ and $\bar{q}_{i,j}$