Lecture 5.
Kinetics and Transport in Sorption (2)

- Solute Movement Theory
  - Derivation of solute wave velocity equation
  - Solute movement diagrams
- Nonideal Concentration Waves
- Effect of Favorable Isotherm on Concentration Waves
  - Shock wave analysis
  - Diffuse wave analysis

Solute Movement Theory (1)

- Where solutes are as they migrate through the column
  - In the mobile fluid (external void volume, $\varepsilon_b A_c \Delta z$)
  - In the stagnant fluid inside particle (internal void volume, $(1-\varepsilon_b)\ \varepsilon_p A_c \Delta z$)
  - Sorbed to the particle

→ The only solutes moving towards the column exit are in the mobile fluid

$$\frac{\textbf{Amount in mobile fluid}}{\textbf{Total amount in segment}}$$

$$= \frac{\textbf{Amount in mobile fluid}}{\textbf{Amount in (mobile fluid + stationary fluid + sorbed)}}$$

- Amount solute increment in mobile fluid

: (volume of column segment) × (fraction which is mobile fluid)

× (increment in concentration)

$$= (\Delta z A_c)(\varepsilon_b)(\Delta c)$$

Solute Movement Theory (2)

$$\frac{\textbf{Amount increment in mobile fluid}}{\textbf{Total amount increment in segment}}$$

$$= \frac{(\Delta z A_c)\varepsilon_b \Delta c}{(\Delta z A_c)\varepsilon_b \Delta c + (\Delta z A_c)(1-\varepsilon_b)\varepsilon_p \Delta c Q_d + (\Delta z A_c)(1-\varepsilon_b)(1-\varepsilon_p)\rho_s \Delta q}$$

Q_d : fraction of volume of pores which a molecule can penetrate

- Average velocity of the solute in the column (solute wave velocity)

$$u_s = u \times (\textbf{fraction solute in mobile phase})$$

$$= u \times \left(\frac{\textbf{amount solute in mobile phase}}{\textbf{total amount solute in column}} \right)$$

$$u_s(T) = \frac{u}{1 + \left[(1-\varepsilon_b)/\varepsilon_b\right]\varepsilon_p Q_d + \left[(1-\varepsilon_b)/\varepsilon_b\right](1-\varepsilon_p)\rho_s\left(\Delta q/\Delta c\right)}$$

Solute Movement Theory (3)

- Assumptions
  - The solid and fluid are locally in equilibrium (ignoring mass transfer effects) → Δq can be related to Δc by equilibrium adsorption isotherm
  - Dispersion and diffusion are negligible → all of the solute travel at the same average solute velocity
- For linear equilibrium, Δq/Δc = k(T)

$$u_s(T) = \frac{u}{1 + \left[(1-\varepsilon_b)/\varepsilon_b\right]\varepsilon_p Q_d + \left[(1-\varepsilon_b)/\varepsilon_b\right](1-\varepsilon_p)\rho_s k(T)}$$

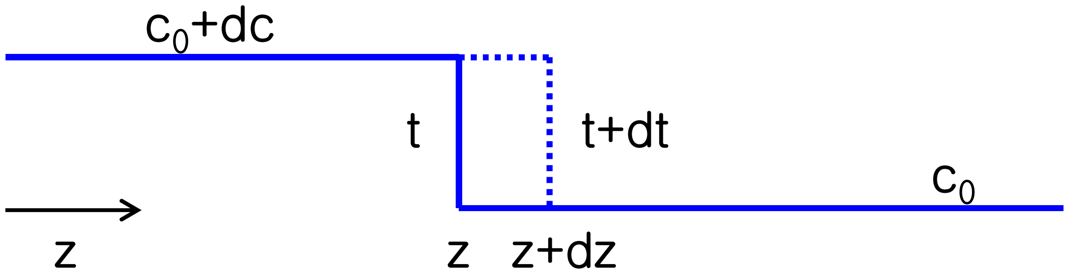
  - The highest possible solute velocity is u (when the molecules are very large and Q_d = k(T) =0)
  - If adsorption is strong, the solute moves slowly
  - When the adsorption equilibrium is linear, the solute velocity does not depend on the solute concentration

Solute Movement Theory (4)

- Different derivation based on differential step disturbance in concentration

The packed column is originally at a solute concentration, c_A (in the interparticle mobile phase)

A differential step in concentration, dc_A, is introduced in the column and moves a distance dz in a time dt



Mass balance to a column element of volume Adz, that is crossed by the concentration step in a time dt

$$\begin{aligned}&(\textbf{solute entering at z duing dt}) = (\textbf{solute living at z + dz duing dt})\\&+(\textbf{solute accumulating in interparticular phase duing dt})\\&+(\textbf{solute adsorbing in intraparicular phase duing dt})\end{aligned}$$

Solute Movement Theory (5)

In mathematical terms,

$$\varepsilon_b A u (dt)(c_A + dc_A)$$

$$= \varepsilon_b A u (dt) c_A + \varepsilon_b A (dz)(dc_A) + \rho (1-\varepsilon_b) A (dz)(dq_A)$$

$$u_s = \frac{dz}{dt} = \frac{u}{1 + \rho \dfrac{1-\varepsilon_b}{\varepsilon_b} \dfrac{dq_A}{dc_A}}$$

- Other expression

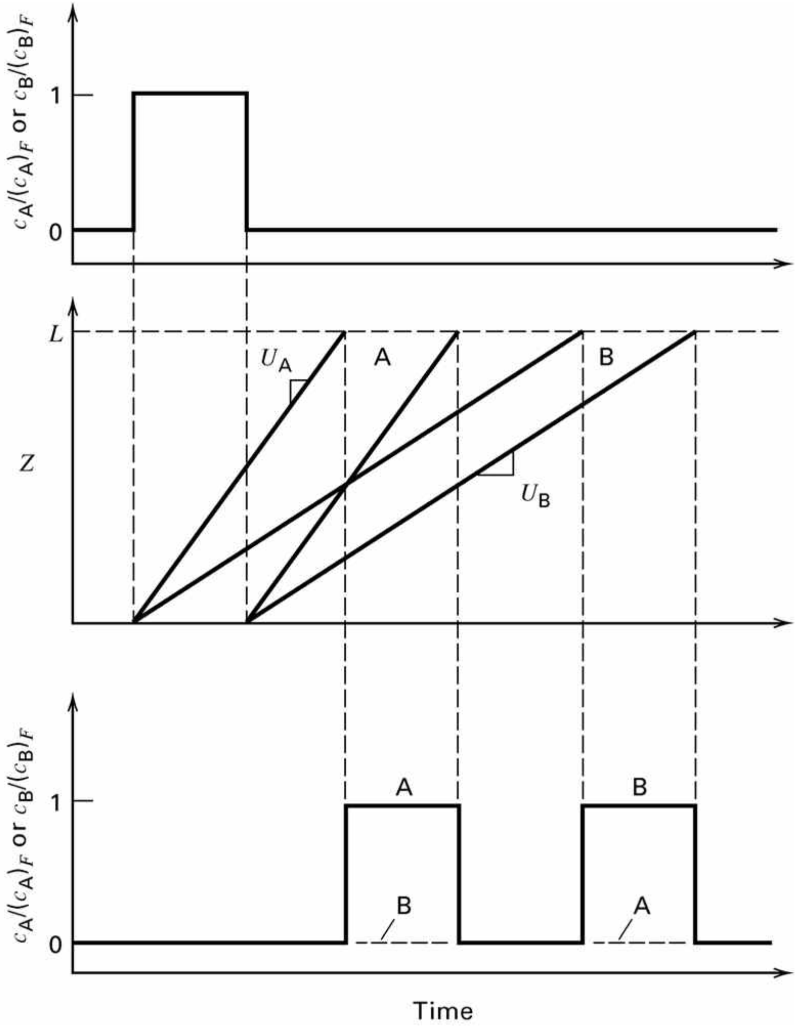
$K_d \gg 1$

$$u_s = \omega u = \frac{u}{1 + \dfrac{1-\varepsilon_b}{\varepsilon_b} \varepsilon_p^* (1 + K_d)} \simeq \frac{u}{1 + \dfrac{1-\varepsilon_b}{\varepsilon_b} \varepsilon_p^* K_d}$$

ω : fraction of solute in the moving fluid phase at equilibrium

Solute Movement Diagrams

- Ideal solute movement model for isothermal chromatography



Feed pulse

Solute movement in column

Product concentration

- Overlapping solute peaks are gradually separated by the fractional difference in migration velocities
- The area under each solute peak is proportional to the mass of the component

[Example] Separation by Pulse Chromatography (1)

An aqueous solution of 3 g/cm^3 each of glucose (G), sucrose (S), and fructose (F) is to be separated in an ion-exchange chromatographic column. The superficial solution velocity, $u_s = \varepsilon_b u$, is 0.031 cm/s and bed void fraction is 0.39. If a 500-second feed pulse, t_p, is followed by elution with pure water, what length of column packing is needed to separate the three solutes if sorption equilibrium is assumed? How soon after the first pulse begins can a second 500-second pulse begin?

Solute	K
Glucose	0.26
Sucrose	0.40
Fructose	0.66

- Interstitial solution velocity

$$u = u_s / \varepsilon_b = 0.031/0.39 = 0.0795\,\mathrm{cm/s}$$

- Wave (migration) velocity

$$u_s = \frac{u}{1 + \dfrac{1-\varepsilon_b}{\varepsilon_b} K_d}$$

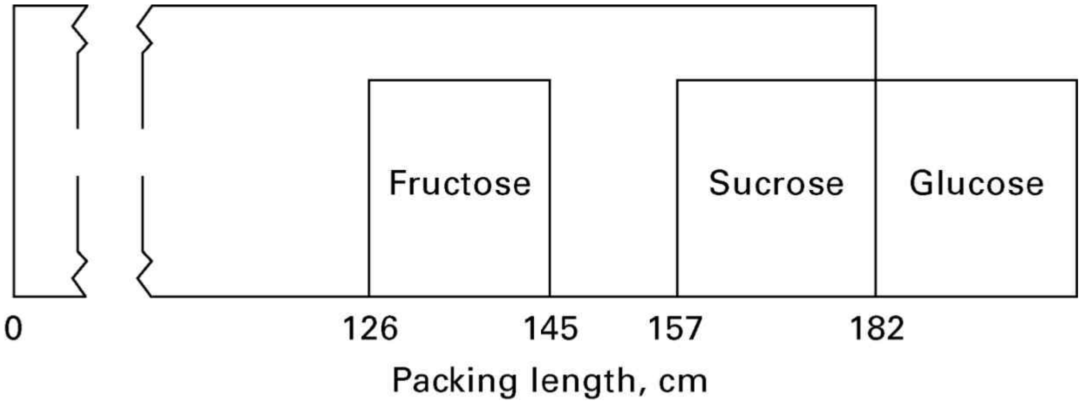
$$u_G = \frac{0.0795}{1 + \left(\dfrac{1-0.39}{0.39}\right)(0.26)} = 0.0565\,\mathrm{cm/s} \quad u_S = 0.0489\,\mathrm{cm/s} \quad u_F = 0.0391\,\mathrm{cm/s}$$

[Example] Separation by Pulse Chromatography (2)

- The smallest difference in wave velocities is between glucose and sucrose, so the separation between these two waves determines the column length
- The minimum column length, assuming equilibrium, corresponds to the time at which the trailing edge of the glucose wave pulse, together with the leading edge of the sucrose wave pulse, leaves the column

$$t_p + \frac{L}{u_G} = \frac{L}{u_S} \qquad 500 + \frac{L}{0.0565} = \frac{L}{0.0489} \qquad \rightarrow L = 182\,\text{cm}$$

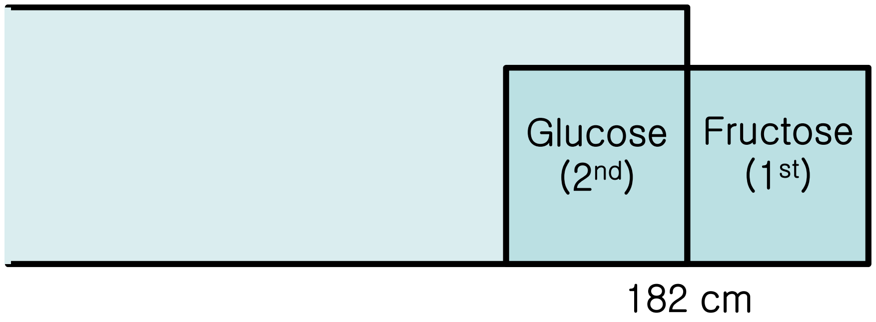
- The glucose just leaves the column at $500 + \dfrac{182}{0.0565} = 3{,}718\,\text{s}$



Locations of solute waves of first pulse at 3,718 s

[Example] Separation by Pulse Chromatography (3)

- The time at which the second pulse begins is determined so that the trailing edge of the first fructose wave pulse just leaves the column as the second pulse of glucose begins to leave the column



Based on the fructose

$$500 + 182/0.0391 = 5,155\,\mathrm{s}$$

Residence time for the leading edge of a glucose wave

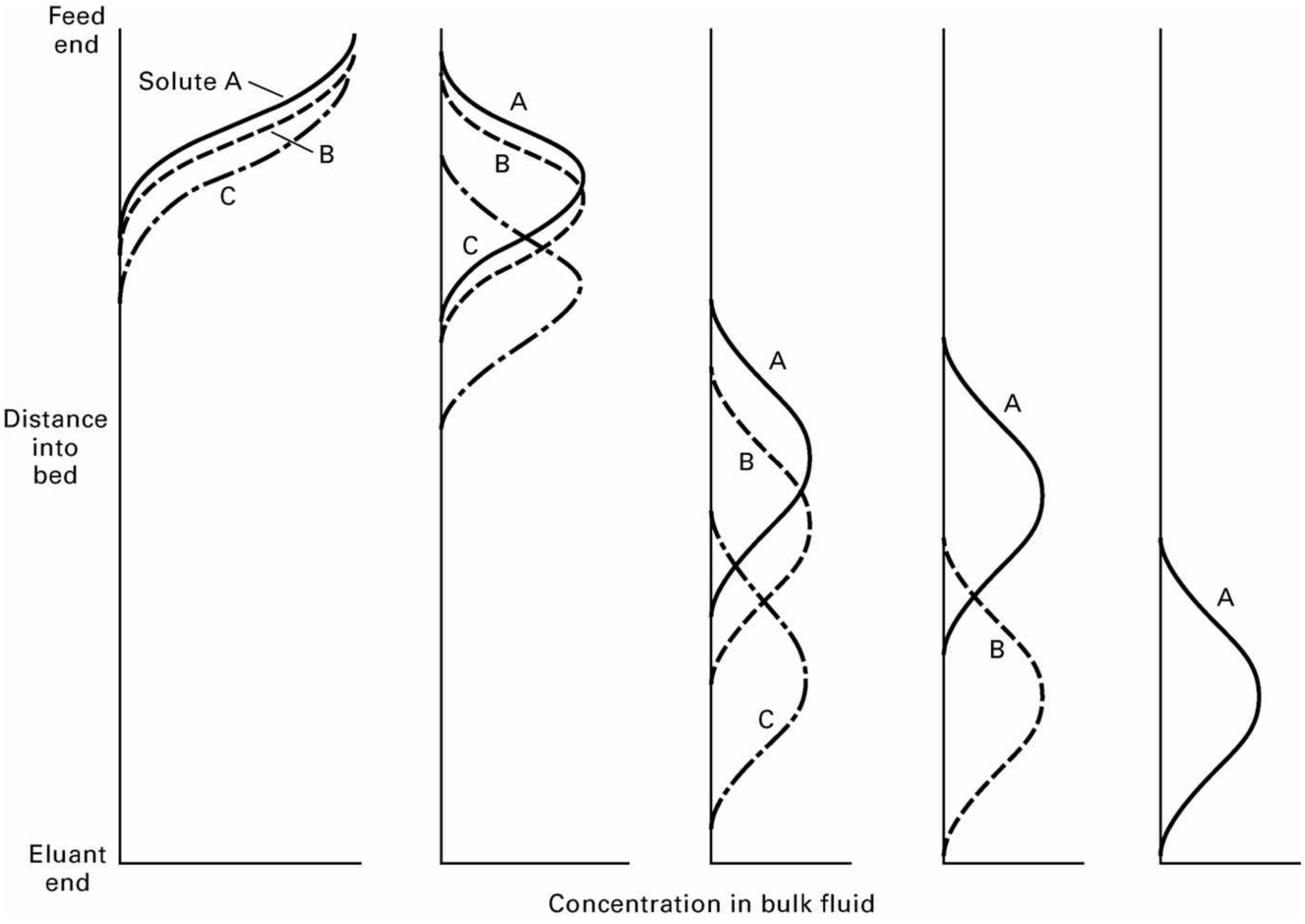
$$182/0.0565 = 3,220\,\mathrm{s}$$

Therefore, the second pulse can begin at 5,155 − 3,220 = 1,935 s

Pulse (500 s) → Elute (1,435 s) → Pulse (500 s) → Elute (1,435 s)

Nonideal Concentration Waves

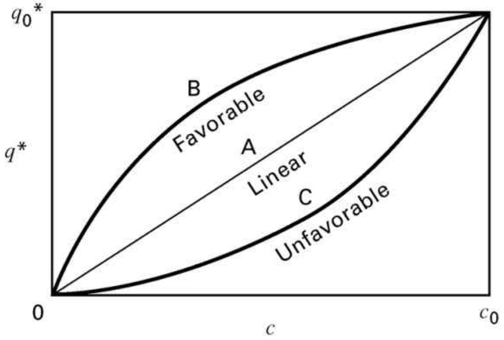
- When mass-transfer resistances, axial dispersion, and/or other nonideal phenomena are not negligible

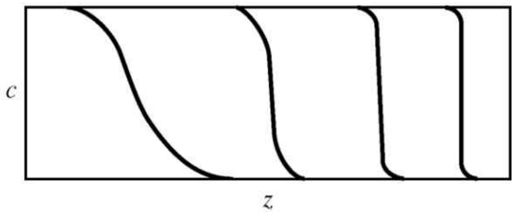


- The effect of mass transfer causes the peaks to overlap significantly
- To obtain a sharp separation, it is necessary to lengthen the column or reduce the feed pulse time, t_F

Effect of Favorable Isotherm on Sharpening Breakthrough

- Self-sharpening wave front





Self-sharpening wave front caused by a favorable adsorption isotherm (constant pattern S-shaped curve)

- For a packed bed of significant capacity ($K_d \gg 1$)

$$u_s = \frac{u}{1+\frac{1-\varepsilon_b}{\varepsilon_b}\varepsilon_p^* K_d} \qquad \alpha = \frac{c_f}{\bar{c}_b} = \frac{1}{\varepsilon_p^*(1+K_d)}$$

  - For a favorable isotherm, solute velocity is relatively small at lower c_f (higher K_d) but increases as c_f increases
  - Lagging wave-front regions at higher solute concentration move faster than leading wave-front regions at lower solute concentration

  → Self-sharpening of breakthrough curves

Shock Wave Analysis (1)

- A mass balance for period Δt over segment Δz

$$\mathbf{(In)\text{-}(Out)\text{-}(Accumulation)=0}$$

$$\varepsilon_b A u(\Delta t)(c_2-c_1)-\left[\varepsilon_b+Q_d\varepsilon_p(1-\varepsilon_p)\right](c_2-c_1)A\Delta z$$
$$-(1-\varepsilon_b)(1-\varepsilon_p)\rho_s(q_2-q_1)A\Delta z=0$$

where 1 refers to conditions before the shock wave and 2 to after the shock

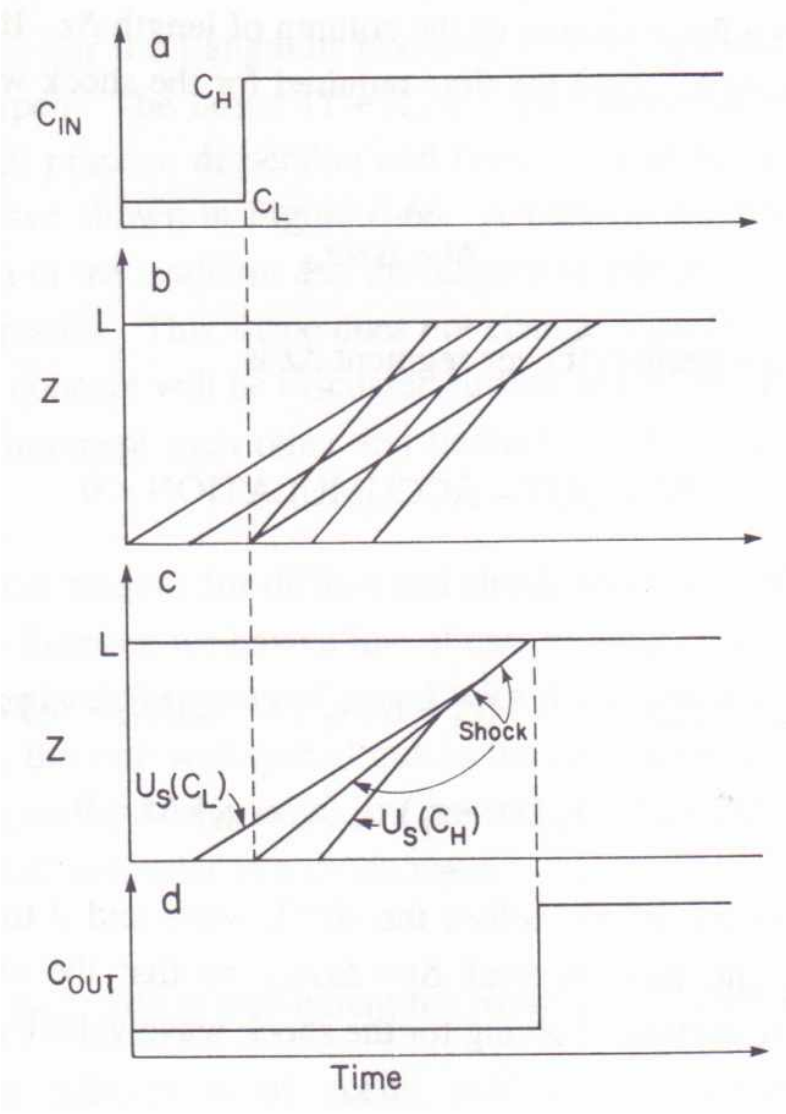
Select the time interval $\Delta t=\Delta z/u_{sh}$ so that the shock wave passes through the entire section

- Shock wave velocity

$$u_{sh}=\frac{u}{1+\left[(1-\varepsilon_b)/\varepsilon_b\right]\varepsilon_p Q_d+\left[(1-\varepsilon_b)/\varepsilon_b\right](1-\varepsilon_p)\rho_s\left[(q_2-q_1)/(c_2-c_1)\right]}$$

The more the curvature of the isotherm, the stronger the tendency for the shock wave to sharpen

Shock Wave Analysis (2)



Inlet concentration

Physically impossible solute waves

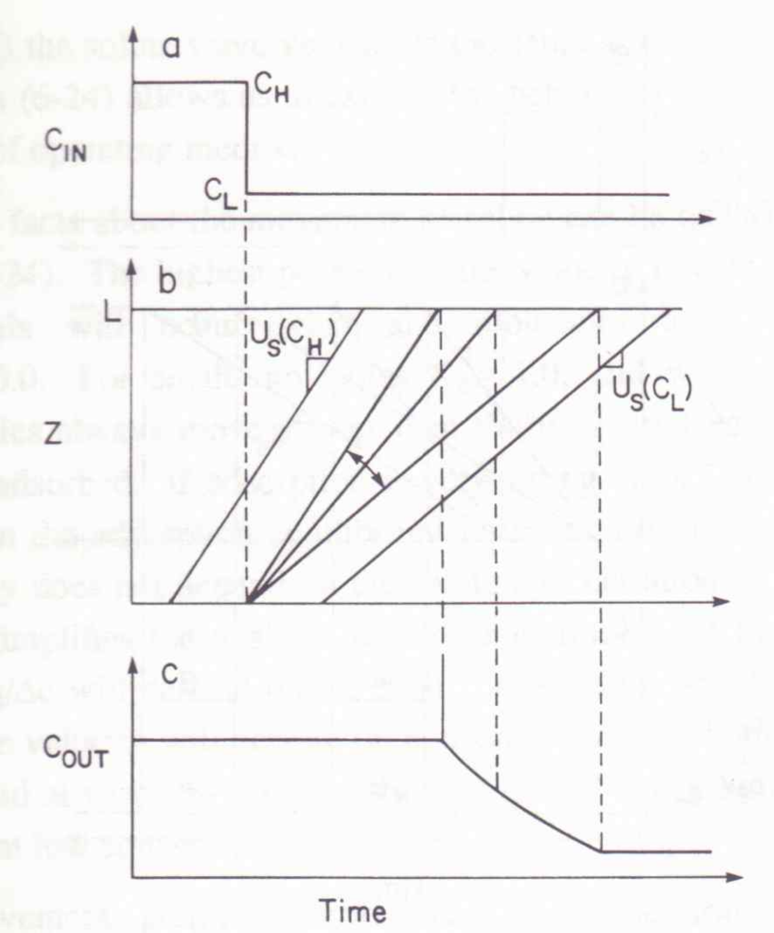
Shock wave

$$u_s\ (c_{high}) > u_{sh} > u_s\ (c_{low})$$

Outlet concentration

Diffuse Wave Analysis

- A diffuse wave occurs when a concentrated solution is displaced by a dilute solution



Inlet concentration

Solute movement

Outlet concentration

The spreading is due to the shape of the isotherms and is proportional to the distance traveled (proportional pattern)

$$\lim_{\Delta c \to 0} \frac{\Delta q}{\Delta c} = \left. \frac{\partial q}{\partial c} \right|_T$$