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) **Solute Movement Theory**
 Amount is a start of the Solutes are as they migrate through the colure mobile fluid (external void volume, $\epsilon_b A_c \Delta z$ **)

e stagnant fluid inside particle (internal void volumed to the particle
 Solute Movement Theory (**
 E solutes are as they migrate through the column

the mobile fluid (external void volume, $\varepsilon_b A_c \Delta z$)

the stagnant fluid inside particle (internal void volume, (1

bed to the particle

a on

- 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-ε_b) ε_pA_c∆z)
	- Sorbed to the particle
- \rightarrow The only solutes moving towards the column exit are in the mobile fluid **Allengths**

As they migrate through the column

external void volume, $\epsilon_b A_c \Delta z$)

d inside particle (internal void volume, $(1-\epsilon_b) \epsilon_p A_c \Delta z$)

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oving towards the column exit are in the mobile fluid
 **Amount in mobile Solutes are as they migrate through the column

mobile fluid (external void volume,** $\varepsilon_b A_c \Delta z$ **)

stagnant fluid inside particle (internal void volume,** $(1-\varepsilon_b) \varepsilon_p A_c \Delta z$ **)

ad to the particle

only solutes moving towar**

Amount in mobile fluid
Amount in (mobile fluid + stationary fluid + sorbed)

- Amount solute increment in mobile fluid
- : (volume of column segment) \times (fraction which is mobile fluid) The only solutes moving towards the column exit are in t
 $\frac{\text{Amount in mobile fluid}}{\text{Total amount in segment}}$
 $=\frac{\text{Amount in mobile fluid}}{\text{Amount in (mobile fluid + stationary fluid + sorbed)}}$

smount solute increment in mobile fluid

(volume of column segment) × (fraction which is mol
 \times (increment in

 \times (increment in concentration)

Solute Movement Theory (2) **Solute Movement Theory (2**
Amount increment in mobile fluid
Fotal amount increment in segment
 $= \frac{(\Delta z A_c) \varepsilon_b \Delta c}{(4.4 \lambda) (4.4 \lambda (1 - \lambda) (4.$

Solute Movement Theory (2)
Amount increment in mobile fluid
Total amount increment in segment
 $=\frac{(\Delta z A_c)\varepsilon_b\Delta c}{(\Delta z A_c)\varepsilon_b\Delta c+(\Delta z A_c)(1-\varepsilon_b)\varepsilon_p\Delta c Q_d+(\Delta z A_c)(1-\varepsilon_p)(1-\varepsilon_p)\rho_s\Delta q}$ **ement Theory (2)**
 efluid
 $\frac{(\Delta z A_c) \varepsilon_b \Delta c}{\Delta z}$
 $\frac{(\Delta z A_c) \varepsilon_b \Delta c}{\Delta z}$
 $\frac{(\Delta z A_c) \varepsilon_b \Delta c}{\Delta z}$
 Sores which a molecule can penetrate Solute Movement Theory (2)

mount increment in mobile fluid

tal amount increment in segment
 $(\Delta z A_c) \varepsilon_b \Delta c$
 $(\Delta z A_c) \varepsilon_b \Delta c + (\Delta z A_c)(1 - \varepsilon_b) \varepsilon_p \Delta c Q_d + (\Delta z A_c)(1 - \varepsilon_b)(1 - \varepsilon_p) \rho_s \Delta q$
 Q_d: fraction of volume of pores $\mathcal{E}_i \Delta \mathcal{C}$ **Olute Movement Theory (2)**

<u>Externant in mobilefluid</u>

 $\frac{(\Delta z A_c)\varepsilon_b\Delta c}{\varepsilon_b\Delta c+(\Delta z A_c)(1-\varepsilon_b)\varepsilon_p\Delta c\mathcal{Q}_d+(\Delta z A_c)(1-\varepsilon_p)(1-\varepsilon_p)\rho_s\Delta q}$
 raction of volume of pores which a molecule can penetrate

velocity of the s **ement Theory (2)**

fluid
 $\frac{\text{fluid}}{\text{gment}}$
 $\frac{\Delta z A_c \right) \varepsilon_b \Delta c}{\Delta \varepsilon_p \Delta c Q_d + (\Delta z A_c)(1-\varepsilon_p)(1-\varepsilon_p)\rho_s \Delta q}$

pres which a molecule can penetrate **Solute Movement Theory (2)**

mount increment in mobile fluid

tal amount increment in segment
 $(\Delta z A_c)\varepsilon_b \Delta c$
 $(\Delta z A_c)\varepsilon_b \Delta c + (\Delta z A_c)(1 - \varepsilon_b)(1 - \varepsilon_b)(1 - \varepsilon_b)\rho_s \Delta q$
 Q_a: fraction of volume of pores which a molecule ca **nent Theory (2**
 $\frac{d}{dt}$
 $\frac{d}{dt}$
 $c \mathcal{Q}_d + (\Delta z A_c)(1-\varepsilon_b)(1-\varepsilon_p)$ **Solute Movement Theory (2)**

 c intercement in mobile fluid

 $\frac{(\Delta z A_c)\varepsilon_b\Delta c}{\kappa_c\delta\kappa_b\Delta c+(\Delta z A_c)(1-\varepsilon_b)\varepsilon_p\Delta c}$
 $\frac{(\Delta z A_c)(1-\varepsilon_b)(1-\varepsilon_b)(1-\varepsilon_p)\rho_s\Delta q}{\kappa_c\delta\kappa_b\Delta c}$
 $\frac{d\Delta z}{dt}$
 $\frac{d\Delta z}{dt}$ is fraction of vol **Solute Movement Theory (2)**
 OUTE MOVEMENT Theory (2)
 OUTE:
 EXA, $\frac{(\Delta z A_c) \varepsilon_b \Delta c}{\Delta \varepsilon_c \Delta c + (\Delta z A_c)(1 - \varepsilon_b) \varepsilon_p \Delta c Q_d + (\Delta z A_c)(1 - \varepsilon_b)(1 - \varepsilon_p) \rho_s \Delta q}$
 OUTE:
 PA is fraction of volume of pores which a molecul $=$ $\frac{1}{(1-1)^2}$ **ife Movement Theory (2)**
 Interment in mobile fluid

increment in segment
 $(\Delta z A_c)\varepsilon_b \Delta c$
 $+(\Delta z A_c)(1-\varepsilon_b)\varepsilon_p \Delta c Q_d + (\Delta z A_c)(1-\varepsilon_b)(1-\varepsilon_p)\rho_s \Delta q$

In of volume of pores which a molecule can penetrate

ity of the solute in mount increment in mobile fluid

tal amount increment in segment
 $(\Delta z A_c) \varepsilon_b \Delta c$
 $(\Delta z A_c) \varepsilon_b \Delta c + (\Delta z A_c)(1 - \varepsilon_b) \varepsilon_p \Delta c Q_d + (\Delta z A_c)(1 - \varepsilon_b)(1 - \varepsilon_p) \rho_s \Delta q$
 Q_a : fraction of volume of pores which a molecule can penetrate
 areforment in mobile fluid
 $\frac{(\Delta z A_c) \varepsilon_b \Delta c}{\Delta c + (\Delta z A_c)(1 - \varepsilon_b) \varepsilon_p \Delta c Q_d + (\Delta z A_c)(1 - \varepsilon_b)(1 - \varepsilon_p) \rho}$
 a tion of volume of pores which a molecule can penetrate

ocity of the solute in the column (solute wave

fractio

 \boldsymbol{Q}_d : fraction of volume of pores which a molecule can penetrate \vert

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

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

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

amount increment in mobile fluid

\ntotal amount increment in segment

\n
$$
(\Delta z A_c) \varepsilon_b \Delta c
$$
\n
$$
(\Delta z A_c) \varepsilon_b \Delta c + (\Delta z A_c)(1 - \varepsilon_b) \varepsilon_p \Delta c Q_d + (\Delta z A_c)(1 - \varepsilon_b)(1 - \varepsilon_p) \rho_s \Delta q
$$
\n
$$
Q_d: \text{fraction of volume of pores which a molecule can penetrate}
$$
\nerage velocity of the solute in the column (solute wave velocity)

\n
$$
u_s = u \times (\text{fraction solute in mobile phase})
$$
\n
$$
= u \times \left(\frac{\text{amount solute in mobile phase}}{\text{total amount solute in column}}\right)
$$
\n
$$
u_s(T) = \frac{u}{1 + \left[(1 - \varepsilon_b)/\varepsilon_b\right] \varepsilon_p Q_d + \left[(1 - \varepsilon_b)/\varepsilon_b\right](1 - \varepsilon_p) \rho_s (\Delta q / \Delta c)}
$$

Solute Movement Theory (3)

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

Solute Movement Theory (3)\nImptions

\nis solid and fluid are locally in equilibrium (ignoring mass transfer sets)
$$
\rightarrow
$$
 Δq can be related to Δc by equilibrium adsorption isotherm

\nexpression and diffusion are negligible \rightarrow all of the solute travel at the

\nlinear equilibrium, $\Delta q/\Delta c = k(T)$

\n $u_s(T) = \frac{u}{1 + \left[(1 - \varepsilon_b)/\varepsilon_b\right] \varepsilon_p Q_d + \left[(1 - \varepsilon_b)/\varepsilon_b\right](1 - \varepsilon_p)\rho_s k(T)}$ \nbe highest possible solute velocity is u (when the molecules are very)

\nis at the mass of the solute moves slowly

- *The CHT THEOTY* (3)
 Q in equilibrium (ignoring mass transfer

to Δc by equilibrium adsorption isotherm

negligible \rightarrow all of the solute travel at the
 $c = k(T)$
 $\frac{u}{Q_d + [(1 \varepsilon_b)/\varepsilon_b](1 \varepsilon_p)\rho_s k(T)}$

elocity is u $-$ 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, $\rm c_A$ (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

-
-

Solute Movement Theory (5)

In mathematical terms,

Solute Movenent Theory (5)
\nmathematical terms,
\n
$$
\varepsilon_b A u(dt) c_A + d c_A)
$$
\n
$$
= \varepsilon_b A u(dt) c_A + \varepsilon_b A(dz) (dc_A) + \rho (1 - \varepsilon_b) A(dz) (dq_A)
$$
\n
$$
u_s = \frac{dz}{dt} = \frac{u}{1 + \rho \frac{1 - \varepsilon_b}{\varepsilon_b} \frac{dq_A}{dc_A}}
$$
\ner expression
\n
$$
u_s = \omega u = \frac{u}{1 + \frac{1 - \varepsilon_b}{\varepsilon_b} \varepsilon_p^* (1 + K_d)} = \frac{u}{1 + \frac{1 - \varepsilon_b}{\varepsilon_b} \varepsilon_p^* K_d}
$$
\n
$$
\omega: \text{fraction of solute in the moving fluid phase at equilibrium}
$$

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

• Other expression

$$
u = 1 + \rho \frac{1 - \epsilon_b}{\epsilon_b} \frac{u_A}{dc_A}
$$

er expression

$$
u_s = \omega u = \frac{u}{1 + \frac{1 - \epsilon_b}{\epsilon_b} \epsilon_p^* (1 + K_d)} = \frac{u}{1 + \frac{1 - \epsilon_b}{\epsilon_b} \epsilon_p^* K_d}
$$

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

Solute Movement Diagrams

• Ideal solute movement model for isothermal chromatography

[Example] Separation by Pulse Chromatography (1)

An aqueous solution of 3 $g/cm³$ each of glucose (G), sucrose (S), and fructose (F) is to be separated in an ion-exchange chromatographic column. The superficial solution velocity, $u_s = \epsilon_b u$, 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? **Example 10** Controller and the *u* search of glucose (G), sucrose (S), and ed in an <u>ion-exchange chromatographic</u> tition velocity, $u_s = \varepsilon_b u$, is 0.031 cm/s and a 500-second feed pulse, t_p , is followed by t length of raction is 0.39. If a 500-second feed pulse, t_p, is followed by
h pure water, what length of column packing is needed to
ne three solutes if sorption equilibrium is assumed? How soon
rst pulse begins can a second 500-se **ITADITY (1)**

of glucose (G), sucrose (S), and

on-exchange chromatographic

ity, $u_s = \epsilon_b u$, is 0.031 cm/s and

cond feed pulse, t_p , is followed by

f column packing is needed to

equilibrium is assumed? How soon

and

• Interstitial solution velocity

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

• Wave (migration) velocity

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

 \mathcal{E}_t *b* . .0565 cm/s three solutes if sorption equilibrium is assumed? However three solutes if sorption equilibrium is assumed? Hourse begins can a second 500-second pulse begins $u = u_s/\varepsilon_b = 0.031/0.39 = 0.0795 \text{ cm/s}$
 $u = u_s/\varepsilon_b = 0.031/0.39 =$ **1 0 39 1 0 26** For the time solution is as
 11.1 Solution velocity
 12.26 11.1 Solution velocity
 14.39 = 0.031/0.39 = 0.040
 14.39 = 1
 14.39 $u_s = \frac{u}{1 + \frac{1 - \varepsilon_b}{\varepsilon_b}} K_d$
 14.39 = 0.0565 cm/s $u_s = 0.0489$ cm
 14.39 = **bed vold Haction is 0.59. H a 300-second feed pluse,** t_p **, is followed
elution with pure water, what length of column packing is needed
separate the three solutes if sorption equilibrium is assumed? How
after the first p** rate the three solutes if sorption equilibrium is assum
the first pulse begins can a second 500-second puls
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\cdot \text{Interval} \\
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pullibrium is assumed? How soon

d 500-second pulse begin?

blution velocity
 0.031/0.39 = 0.0795 cm/s

tion) velocity
 $\frac{\varepsilon_b}{\varepsilon_b} K_d$
 $\frac{\varepsilon_b}{\varepsilon_d} K_d$

[Example] Separation by Pulse Chromatography (2) **Chromatography (2)**
 Chromatography (2)
 **est difference in wave velocities is between glu

so the separation between these two waves det

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num column length, assuming equilibrium, correction

ich the trailing edg Example] Separation by**
 Chromatography (2
 Chromatography (2
 Chromatography (2
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 Chromatography (2
 Chromatography
 Conduct the Supper Separation
 **Conduct to the Sucrose wave pulse, lea Conserved Separation Sy Pulse

Lead Conserved Synchic Conservance** and

between these two waves determines the

th, assuming equilibrium, corresponds to the

dge of the glucose wave pulse, together with

crose wave puls

- 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 his coparation botwoon that

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um column length, assuming

ich the trailing edge of the glu

g edge of the sucrose wave pl
 $\frac{L}{G} = \frac{L}{u_s}$ 500 + $\frac{L}{0.0565} = \frac{L}{0.0565}$

se just leaves the column at **Chromatography (2)**

lest difference in wave velocities is between glu

so the separation between these two waves de

ength

num column length, assuming equilibrium, correction

hich the trailing edge of the glucose wave **Separation by Puise**
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We velocities is between glucose and

etween these two waves determines the

assuming equilibrium, corresponds to the

e of the glucose wave pulse, together with

Dose wave pulse, leaves the column
 L **1922**

So is between glucose and

se two waves determines the

equilibrium, corresponds to the

ucose wave pulse, together with

ulse, leaves the column
 L
 L
 $L = 182 \text{ cm}$
 $500 + \frac{182}{0.0565} = 3,718 \text{ s}$
 $L = 182$ **DITY (Z)**

s between glucose and

two waves determines the

uilibrium, corresponds to the

se wave pulse, together with

e, leaves the column
 $\frac{1}{99}$ $\rightarrow L = 182 \text{ cm}$
 $+\frac{182}{0.0565} = 3,718 \text{ s}$
 $\frac{1}{99}$ Location

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

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

[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 **500 182 0 0391 5 155s** + = . ,

182 cm

Based on the fructose

Residence time for the leading edge of a glucose wave

Therefore, the second pulse can begin at $5,155 - 3,220 = 1,935$ 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

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

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

\n
$$
u_s = \frac{u}{1 + \frac{1 - \varepsilon_b}{\varepsilon_b} \varepsilon_p^* K_d} \qquad \alpha = \frac{c_f}{\overline{c}_b} = \frac{1}{\varepsilon_f^*(1 + K_d)}
$$
\nfor a favorable isotherm, solute velocity is relatively small at low-

- 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
- \rightarrow Self-sharpening of breakthrough curves

Shock Wave Analysis (1)

• A mass balance for period ∆t over segment ∆z

Shock Wave Analysis (1)
\nmass balance for period
$$
\Delta t
$$
 over segment Δz
\n(In) - (Out) - (Accumulation) = 0
\n
$$
\varepsilon_b A u(\Delta t) (c_2 - c_1) - \left[\varepsilon_b + Q_d \varepsilon_p (1 - \varepsilon_p)\right] (c_2 - c_1) A \Delta z
$$
\n
$$
-(1 - \varepsilon_b)(1 - \varepsilon_p) \rho_s (q_2 - q_1) A \Delta z = 0
$$
\nwhere 1 refers to conditions before the shock wave and 2 to after the shock
\nlect the time interval $\Delta t = \Delta z / u_{sh}$ so that the shock wave passes through

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

• Shock wave velocity

$$
\varepsilon_b A u(\Delta t)(c_2 - c_1) - \left[\varepsilon_b + Q_a \varepsilon_p (1 - \varepsilon_p)\right](c_2 - c_1)A\Delta z
$$

-(1 - ε_b)(1 - ε_p) ρ_s (q_2 - q_1) $A\Delta z$ = 0
where 1 refers to conditions before the shock wave and 2 to after the shock
ect the time interval $\Delta t = \Delta z/u_{sh}$ so that the shock wave passes through
entire section
ock wave velocity

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

g more the curvature of the isotherm, the stronger the tendency for
shock wave to sharper

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

Shock Wave Analysis (2)

concentration

Physically impossible solute waves

Shock wave

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

concentration

Diffuse Wave Analysis

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

displaced

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 $\frac{q}{c} = \frac{\partial q}{\partial c}\Big|_T$ preading is due

e shape of the

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prional to the

nce traveled

ortional pattern)
 $\lim_{\epsilon \to 0} \frac{\Delta q}{\Delta c} = \frac{\partial q}{\partial c} \Big|_T$ The spreading is due to the shape of the isotherms and is proportional to the distance traveled (proportional pattern)

$$
\lim_{\Delta c \to 0} \frac{\Delta q}{\Delta c} = \frac{\partial q}{\partial c}\bigg|_T
$$

Outlet concentration