Lecture 4.
Kinetics and Transport in Sorption (1)

- Mass-Transport Processes in Adsorption
- Convection-Dispersion Model
- Modes of Time-Dependent Sorption Operation
- Chromatogram
- Solute Concentration Distribution
- Separation Efficiency
- Chromatography Resolution

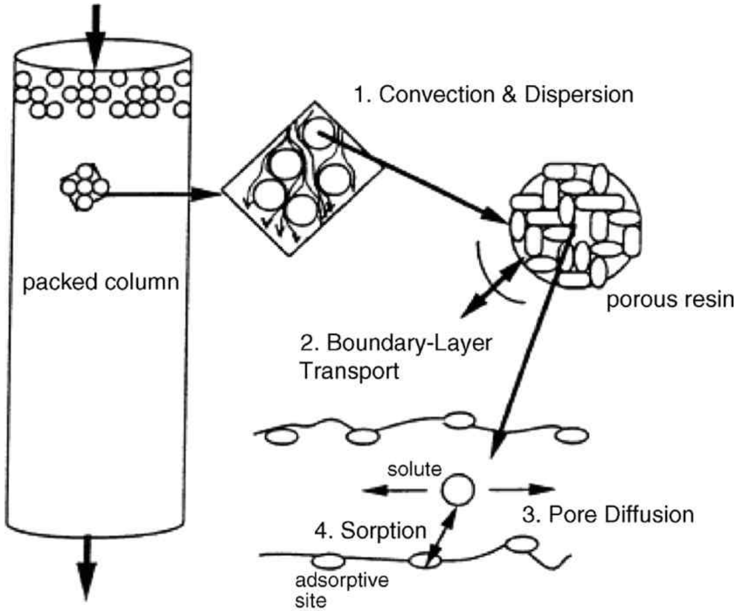
Consecutive Mass–Transport Processes in Adsorption (1)

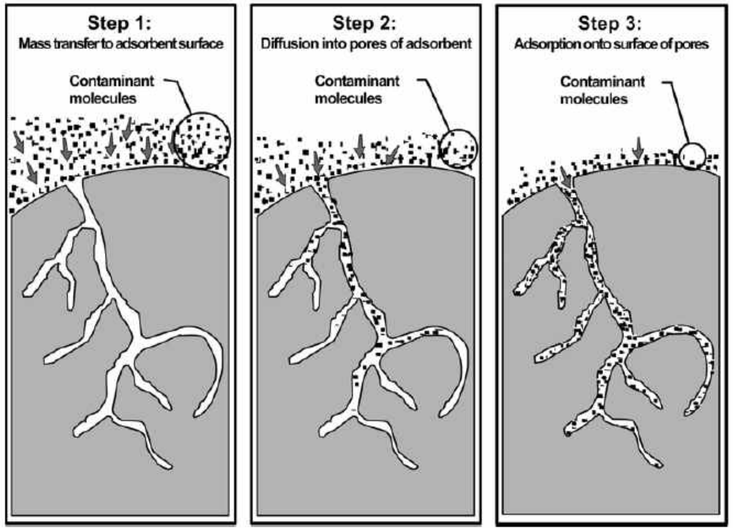
1. Solute transport by bulk flow (convection) and dispersion through interstices of the bed

2. External (interphase) solute transport from the bulk flow to the outer perimeter of the adsorbent through a thin film or boundary layer

3. Internal (intraphase) solute transport by diffusion in quiescent fluid–filled pores

4. Surface diffusion along the internal porous surface of the adsorbent



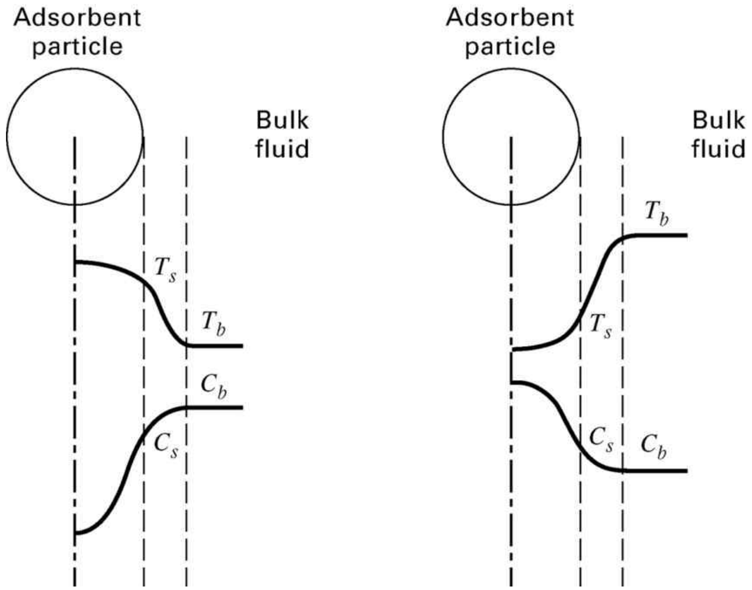


Consecutive Mass-Transport Processes in Adsorption (2)

- External transport
  - Convective dispersion of the solute within the bulk fluid
  - Diffusion though a boundary layer surrounding adsorbent particles
- Axial dispersion of individual solute molecules in the bulk fluid occurs primarily by microscale, fluid-phase phenomena such as mixing via solid obstructions to flow, eddies, and recirculation from regional pressure gradients
- Boundary-layer transport, internal transport, and surface diffusion: random Brownian motion
- Kinetic interaction depends on solute orientation and frequency of surface collisions
  - Instantaneous for physisorption
  - Can become a controlling step for chemisorption (bond formation)

Solute Concentration and Temperature Profiles

- Regeneration of the adsorbent: the reverse of the four steps occurs, following desorption



- Concentration gradient: usually steepest within the particle
  → The major resistance to mass transfer is in the adsorbent particle
- Temperature gradient: usually steepest in the boundary layer surrounding the particle
  → Resistance to heat transfer is mainly external to adsorbent particle

Convection–Dispersion Model (1)

- Fluid-phase concentration $c_f(z,t)$ for solute convected by dispersed, plug flow of fluid at average interstitial velocity u in the axial direction z

$$\frac{\partial c_f}{\partial t}+u\frac{\partial c_f}{\partial z}-E\frac{\partial^2 c_f}{\partial z^2}=-\frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial \bar{c}_b}{\partial t}$$

Change in solute concentration in the bulk fluid with time

Change in c_f with axial location arising from bulk convection

Axial dispersion

Change in solute loading on the stationary phase

ε_b : fractional interstitial void volume (bed porosity)
E : Fickian, convective, axial-dispersion coefficient
$\bar{c}_b$: volume-averaged stationary-phase concentration per unit mass

- For a spherical particle of radius R_p

$$\bar{c}_b=\frac{\int_0^{R_p}(4\pi r^2)c_b dr}{(4/3)\pi R_p^3}=\frac{3}{R_p^3}\int_0^{R_p} r^2 c_b dr$$

* Superficial velocity of the fluid, $u_s = \varepsilon_b u$

Convection–Dispersion Model (2)

- q (equilibrium loading): mass of solute adsorbed on surfaces of the stationary phase per unit mass of adsorbent
- $\bar{c}_b$: both adsorbed solute and unadsorbed solute diffusing in the pore volume of the stationary phase

At equilibrium in nonadsorbing gel–filtration chromatography, q = 0, $\bar{c}_b = \varepsilon_p^* c_f$

- Linear driving force (LDF) approximation

$$\frac{4}{3}\pi R_p^3 \frac{\partial \bar{c}_b}{\partial t} = -k_{c,tot} 4\pi R_p^2 (\bar{c}_b \alpha - c_f)$$

$k_{c,tot}$: overall mass–transfer coefficient

- At equilibrium, solute is partitioned between the bulk fluid and average stationary–phase loading

$$\alpha = \frac{c_f}{\bar{c}_b} = \frac{1}{\varepsilon_p^*(1 + K_d)}$$

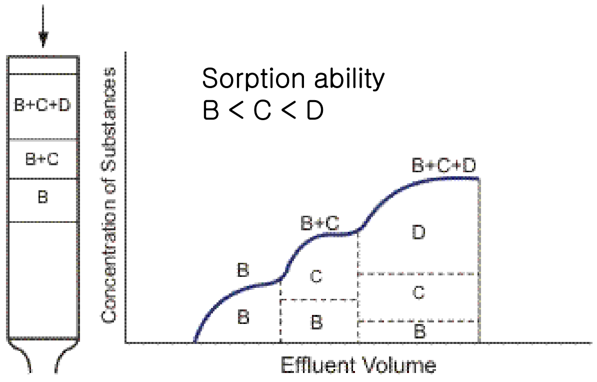
K_d : equilibrium distribution coefficient $K_d = \frac{k_a}{k_d} = \frac{c_s}{c_p}$

ε_p^* : inclusion porosity (effective stationary–phase volume fraction accessible to a specific solute)

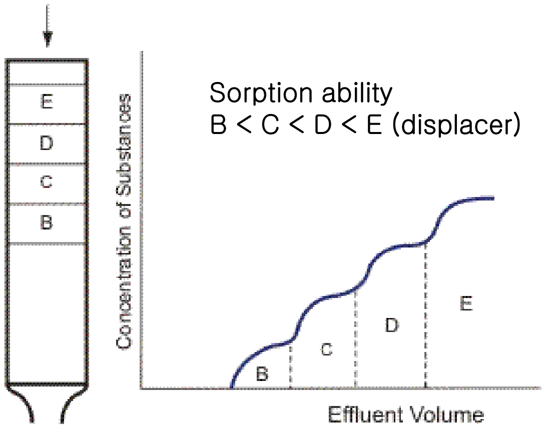
ε_p^* includes only voids penetrable by a particular solute due to size or steric hindrance

Modes of Time-Dependent Sorption Operation

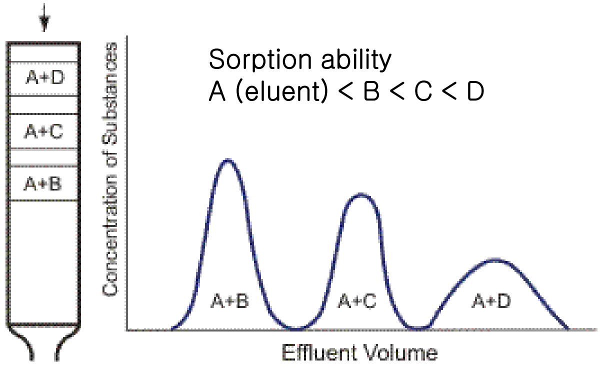
- **Frontal**: The mobile phase (gas or liquid) is fed continuously to the stationary phase until the bed approaches saturation with the solute



- **Displacement**: Following near-saturation of the bed with solute(s), desorption (elution) in consecutive zones of pure substances is effected by substitution with a more strongly adsorbed solute (displacer)



- **Differential (elution)**: A small pulse of solute dissolved in the mobile phase is loaded onto the bed → the solute pulse is carried through the bed (eluted) at a rate lower than pure solvent



Chromatogram (1)

- Retention time: the time elapsed from the moment the sample is fed to the column up to the moment the chromatographic zone of the substance output reaches its maximum

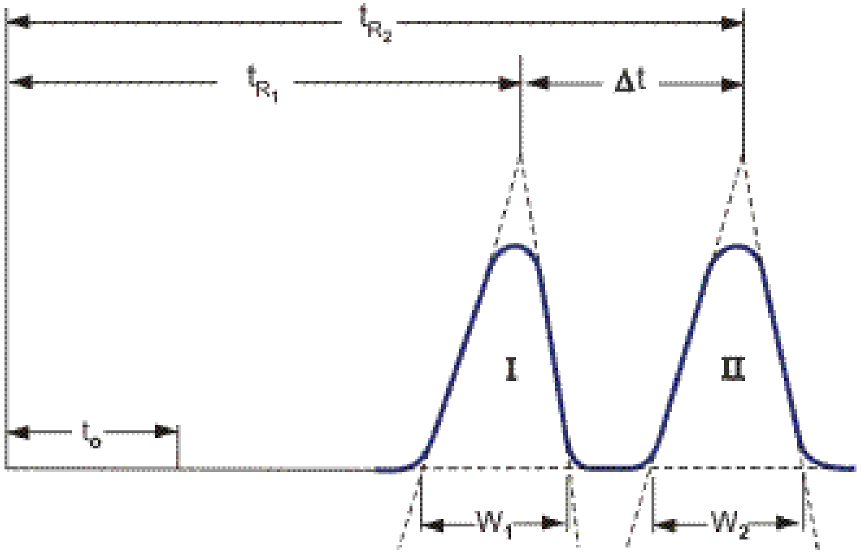
$$t_R = \frac{L}{u_s}$$

u_s : average velocity of solute in column

For pulses which are fairly wide

$$t_R = \frac{L}{u_s} + \frac{t_F}{2}$$

t_F : period of the feed pulse



W = 4σ (σ is the standard deviation of the peak)

- The non-retained peak which exits at t_0 shows when a small, non-retained molecule will exit. t_0 is a measure of the void volume between particles and inside the particles.

Chromatogram (2)

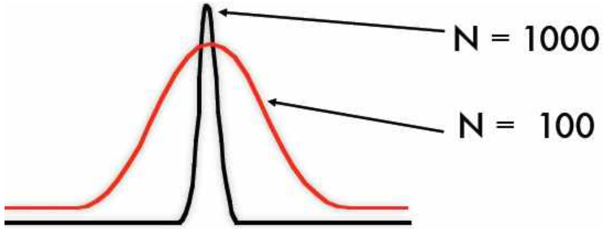
$$\frac{t_{R,2}-t_0}{t_{R,1}-t_0}=\frac{k_2}{k_1}=\alpha_{21}$$

k : equilibrium constant
α_{ij} : selectivity

- Peak sharpness depends on column efficiency, and the distance between the maxima is determined by selectivity
- Efficiency can be expressed quantitatively by N (the number of theoretical chromatographic plates)

$$N=\left(\frac{t_R}{\sigma}\right)^2$$

σ : standard deviation in time unit



- Height of the equivalent theoretical plate

$$H=\frac{L}{N}$$

L : column length

$$H \propto \sigma^2$$

H is proportional to the variance for chromatographic system

Solute Concentration Distribution

- Sharp-pulse input

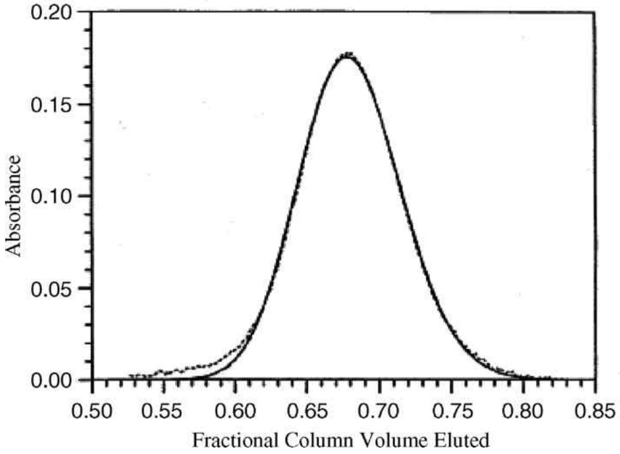
$$c\{z,0\} = \frac{m_0 \delta\{z\}}{A\varepsilon_b}$$

m_0 : solute mass
A : bed cross-sectional area
$\delta\{z\}$: Dirac delta function (zero everywhere except at z=0, where its magnitude is infinity)

- Gaussian solution for eluted peak

$$c = c_{\max} \exp\left(\frac{-x^2}{2\sigma^2}\right)$$

x : deviation from the peak maximum



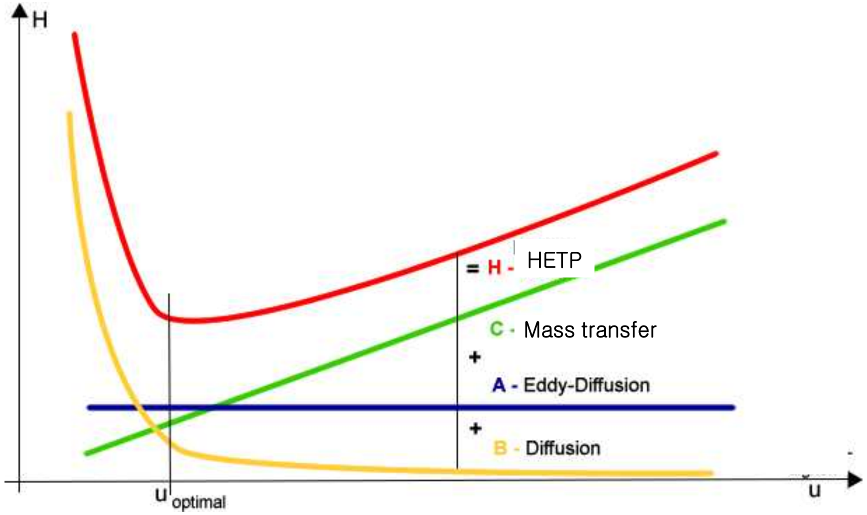
$$c\{z,t\} = \frac{m_0 \omega}{A\varepsilon_b \sqrt{2\pi H z_0}} \exp\left[\frac{-(z-z_0)^2}{2Hz_0}\right]$$

z_0 : mean solute position ($\omega u t$)
ω : fraction of solute in the moving fluid phase at equilibrium

$$\omega = \frac{1}{1 + \frac{1-\varepsilon_b}{\varepsilon_b}\frac{1}{\alpha}}$$

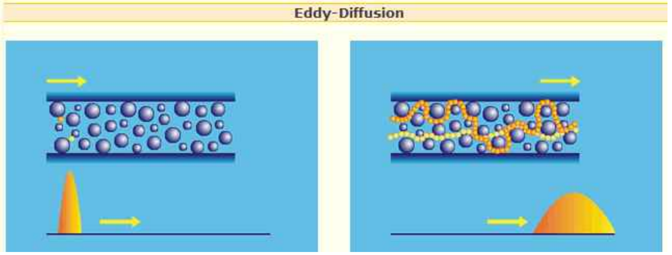
Separation Efficiency (1)

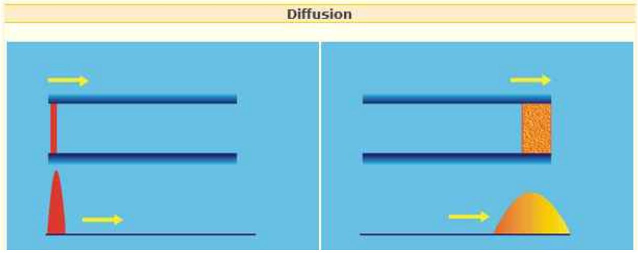
- (Separation efficiency in linear chromatography) $\propto H^{-1}$
- Van Deemter equation



$$H = A + \frac{B}{u} + Cu$$

  - A: eddy-diffusion, related to channeling through a non-ideal packing
  - B: molecular diffusion in the longitudinal direction
  - C: mass transfer resistance between mobile and stationary phases ($C = C_m + C_{sm} + C_s$)





C_m : extraparticle mass transfer (film diffusion)
C_{sm} : diffusion in the stagnant mobile phase (pore diffusion)
C_s : diffusion on the solid

Separation Efficiency (2)

- Relation between H and overall mass-transfer coefficient, $k_{c,tot}$

$$H = 2\left(\frac{E}{u} + \frac{\omega(1-\omega)R_p u}{3\alpha k_{c,tot}}\right)$$

Transport-rate resistance due to convective dispersion

$$\frac{1}{k_{c,tot}} = \frac{1}{k_c} + \frac{R_p}{5\varepsilon_p^* D_e} + \frac{3}{R_p k_a \varepsilon_p^*}\left(\frac{K_d}{1+K_d}\right)^2$$

Resistance in external boundary-layer transport

Resistance in internal intraparticle diffusion

Resistance in kinetic sorption rate

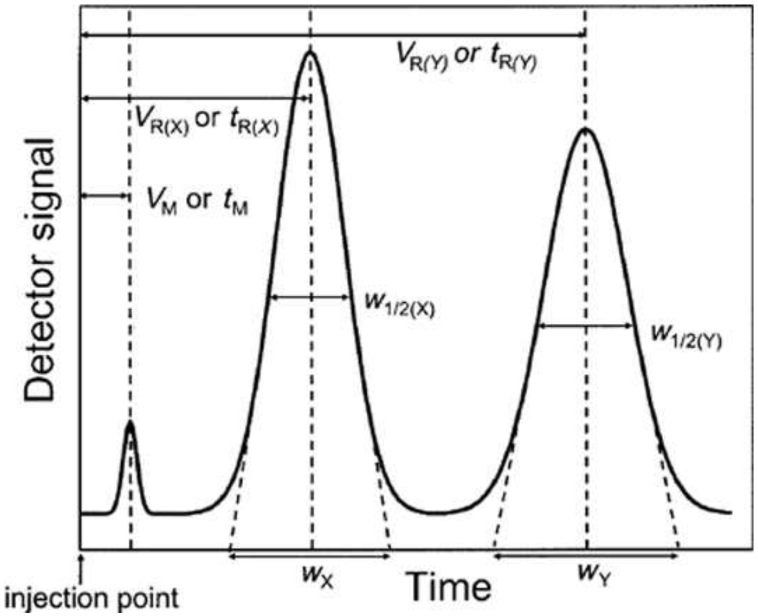
k_c : fluid-phase mass-transfer coefficient
D_e : effective solute diffusivity in the pore liquid

Chromatography Resolution

- Resolution, R: a measure of how completely two neighboring peaks are separated from each other

$$R=\frac{2\left(t_{R,2}-t_{R,1}\right)}{w_1+w_2}$$

$$\begin{cases}\sigma=\dfrac{t_R}{\sqrt{N}}\\ w=4\sigma\end{cases}$$



$$R=\frac{\sqrt{N}\left(t_{R,2}-t_{R,1}\right)}{2\left(t_{R,2}+t_{R,1}\right)}$$

$$R=\frac{\sqrt{N}\left(V_{R,2}-V_{R,1}\right)}{2\left(V_{R,2}+V_{R,1}\right)}$$

Resolution in terms of retention volume