



Spring Semester course

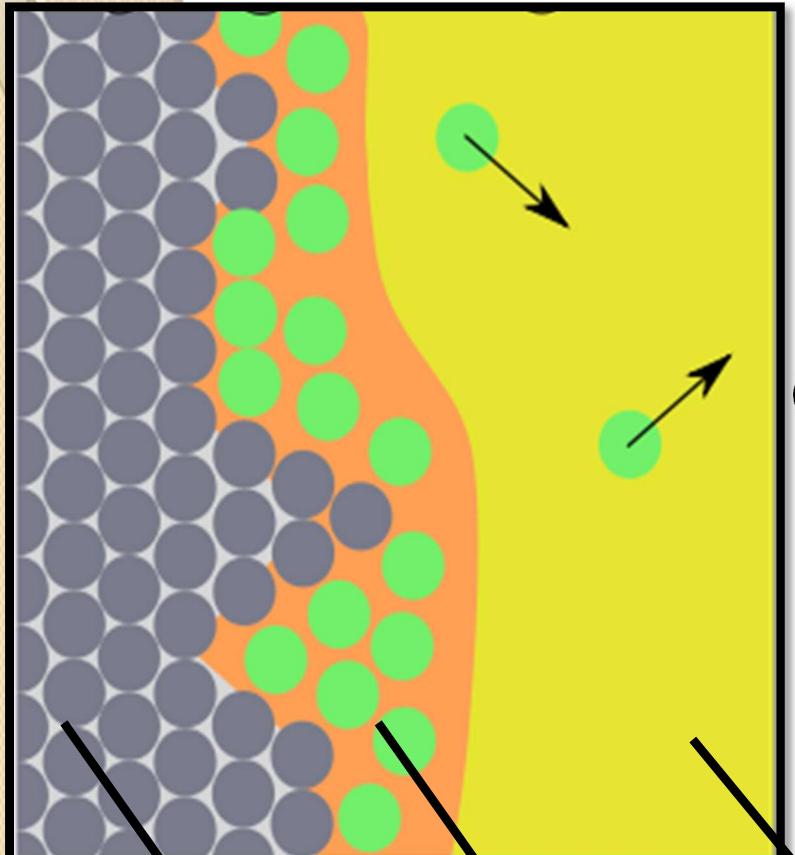
CH31010: Mass Transfer II

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L6: Adsorption

What is Adsorption?



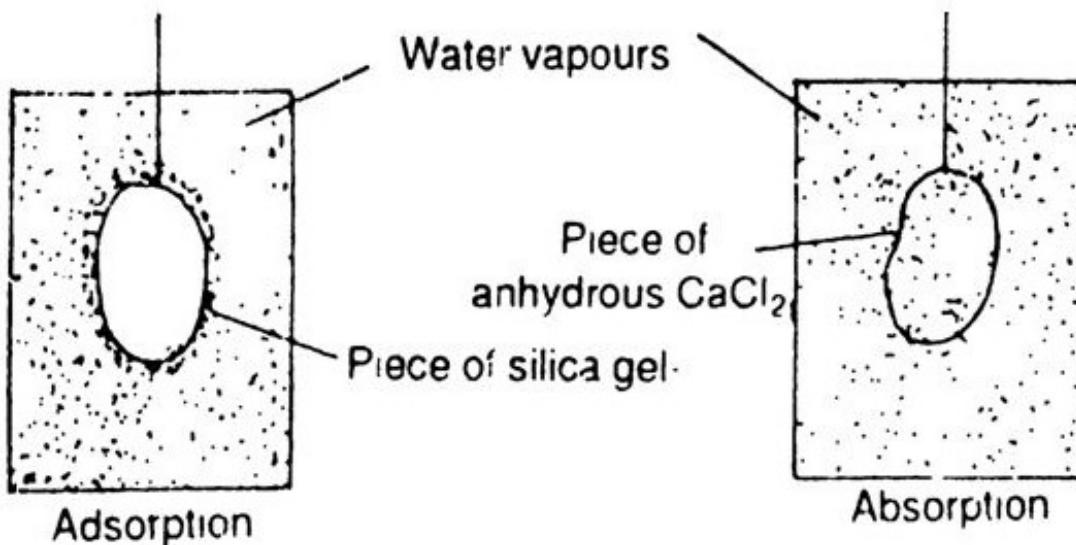
ADSORBENT

ADSORBATE

SOLUTION

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (**adsorbent**), forming a molecular or atomic film (**adsorbate**)

Adsorption	Absorption
It is a surface phenomenon.	It concerns with the whole mass of the absorbent.
In it, the substance is only retained on the surface and does not go into the bulk or interior of the solid or liquid.	It implies that a substance is uniformly distributed, through the body of the solid or liquid.
In it the concentration of the adsorbed molecules is always greater at the free phase.	In it the concentration is low.
It is rapid in the beginning and slows down near the equilibrium.	It occurs at the uniform rate.
Examples : (i) Water vapours adsorbed by silica gel. (ii) NH_3 is adsorbed by charcoal.	Examples : (i) Water vapours absorbed by anhydrous CaCl_2 (ii) NH_3 is absorbed in water forming NH_4OH

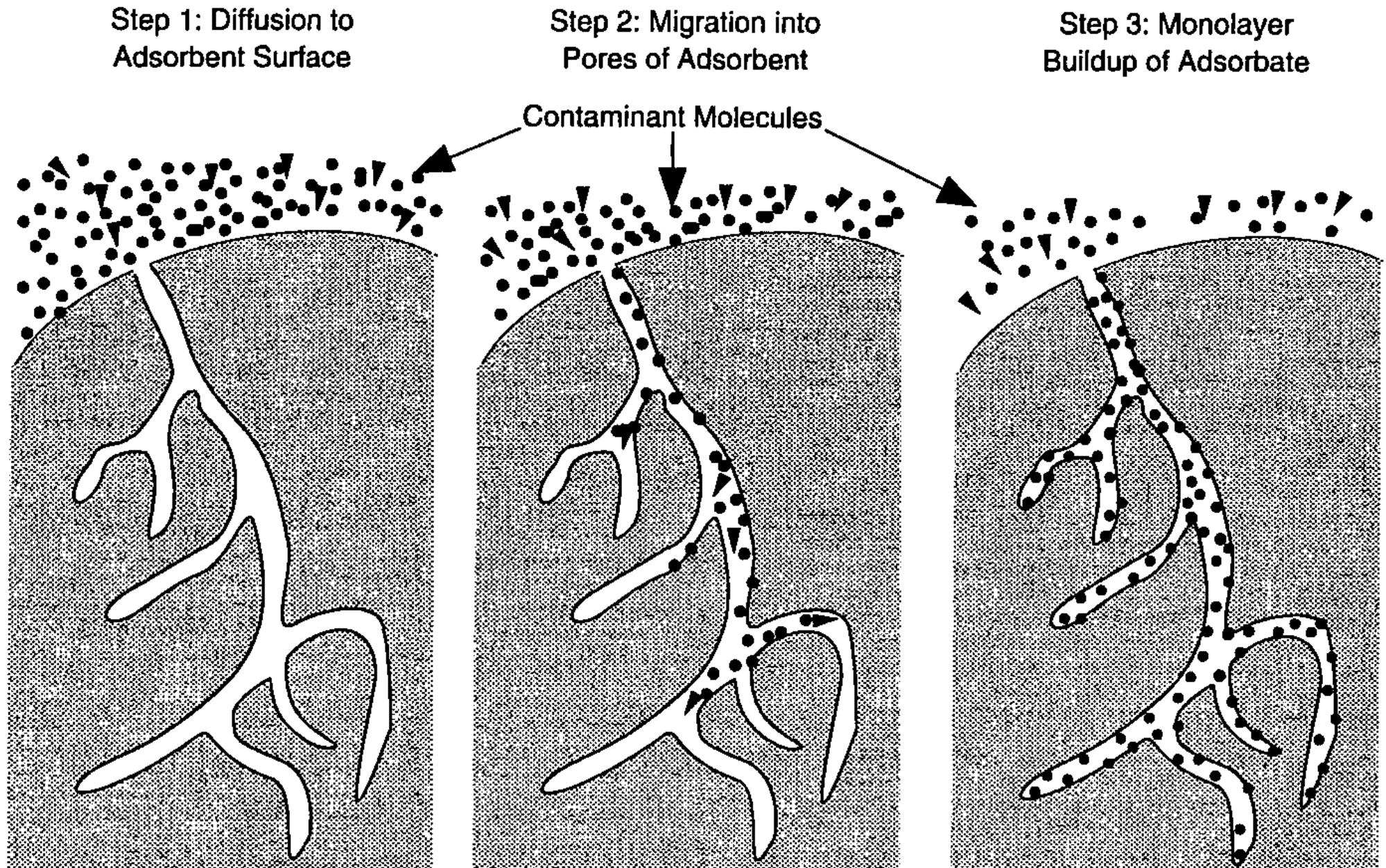


Thus, adsorption is a surface phenomenon while absorption is a bulk property.

The important points of distinction between adsorption and absorption are :

Absorption	Adsorption
1. It is the phenomenon in which the particles of gas or liquid get uniformly distributed throughout the body of the solid.	It is the phenomenon of higher concentration of particles of gas or liquid on the surface than in the bulk of the solid.
2. The concentration is the same throughout the material. Therefore, it is a bulk phenomenon.	The concentration on the surface of the adsorbent is different from that in the bulk. Therefore, it is a surface phenomenon.
3. Absorption occurs at uniform rate.	Adsorption is rapid in the beginning and its rate slowly decreases.

Mechanism of adsorption



Commercially important adsorbents and their characteristics (Keller, 1995)

Adsorbent	Characteristics	Commercial uses	Strengths	Weaknesses
Activated carbon	Hydrophobic surface, favours organics over air or water	Removal of organic pollutants from aqueous or gaseous effluents	Cheapest hydrophobic adsorbent, workhorse of pollution control	Difficult to regenerate if fouling occurs, may catch fire during air regeneration.
Carbon molecular sieve (CMS)	Separates on the basis of difference in intraparticle diffusivity	Production of N ₂ from air	The only practical adsorbent for selective adsorption of O ₂ over N ₂	The only commercial application is in air separation
Silica gel	High capacity hydrophilic adsorbent	Drying of air and other gases	Higher capacity than zeolite molecular sieves (ZMS)	Not very effective if the moisture level has to be reduced to very low
Activated alumina	High capacity, hydrophilic adsorbent	Drying of gas streams	Higher capacity than ZMS	Not as effective as ZMS for the removal of moisture in traces
Zeolite molecular sieve (ZMS)	Hydrophilic surface, polar regular channels	Dehydration, air separation, separation of molecules based on size and shape	Separation of molecules based on both polarity and geometry	Lower adsorption capacity than many other adsorbents
Silicalite	Hydrophobic surface	Removal of organics from gas streams	Can be regenerated by burning more easily	Quite expensive
Polymer adsorbents	Styrene/divinyl benzene copolymer is most common	Removal of organics from gas streams	Less prone to fouling than activated carbon	Much more costly than activated carbon

When to consider adsorption

Distillation, membranes, absorption, liquid-liquid extraction are sometimes viable alternatives.

But adsorption is considered when:

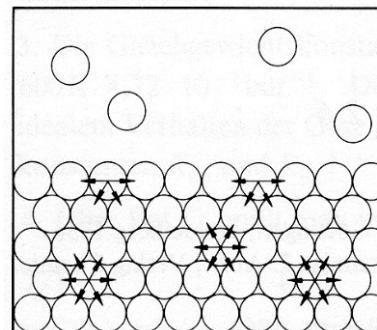
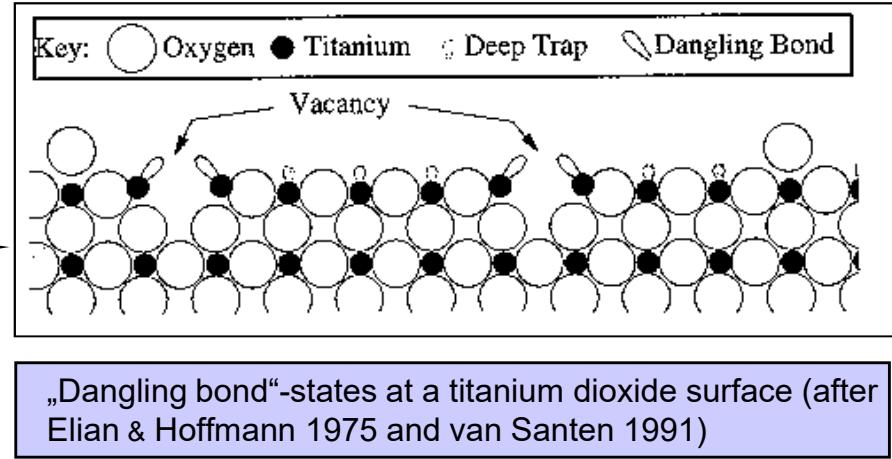
- ▶ relative volatility between components is < 1.5 (e.g. isomers)
- ▶ large reflux ratios would be required
- ▶ too large area for a membrane
- ▶ excessive temperatures or high pressure drops are to be avoided
- ▶ high selectivity is required
- ▶ feed is a very dilute stream of solute (**adsorbate**)

But, some disadvantages:

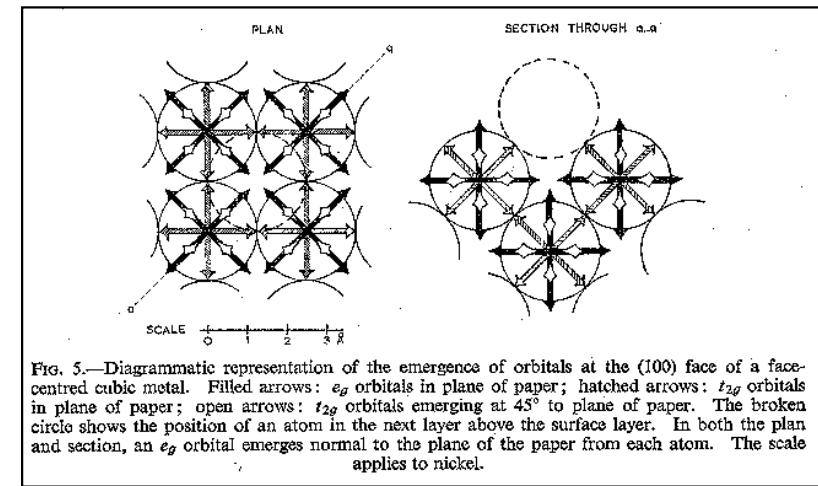
- ▶ only the surface of the adsorbent used
- ▶ regeneration of MSA adsorbent required

The process of adsorption - thermodynamical background

- Altered interaction forces in the region of the phase boundary
- “free” valencies, broken (“dangling”) bonds at the surface
- Nature of interaction forces will depend on the system:
 - a) van-der-Waals (always present),
 - b) ionic (electrostatic),
 - c) covalent,
 - d) metallic
- Strength of the interaction forces for b) ... d) comparable to typical chemical bonds, i.e. between **80** and **300** kJoule/Mol



Asymmetry of the interaction forces in the surface region of a liquid



Directed orbitals on a fcc(100) surface

The process of adsorption – thermodynamical background

Consider the change of free energy (Gibbs Energy G) of a thermodynamical system during any change of state (differential description):

$$dG = \left(\frac{\partial G}{\partial P} \right)_{T,A} dP + \left(\frac{\partial G}{\partial T} \right)_{P,A} dT + \left(\frac{\partial G}{\partial A} \right)_{P,T} dA + \left(\frac{\partial G}{\partial n_i} \right)_{T,P,A} dn_i$$
$$dG = VdP - SdT + \sigma dA + \mu_i dn_i$$

$\left(\frac{\partial G}{\partial P} \right)_{T,A} = +V;$
 $\left(\frac{\partial G}{\partial T} \right)_{P,A} = -S$
 $\left(\frac{\partial G}{\partial A} \right)_{P,T} = \sigma$

with P = pressure, T = temperature, A = surface area, σ = surface tension, V = volume, μ = chemical potential and S = entropy. The third term becomes only important, if the surface area is large in relation to the bulk phase (high degree of dispersion). Example: Raney-Nickel as a catalyst in hydrogenation reactions.

The surface tension is equivalent to the surface energy [Nm/m^2], which governs the macroscopic energetics of both adsorption and desorption phenomena. Since, however, thermodynamics is a *continuum* description of the chemical state of systems, it is unable to describe or predict *microscopic* details or elementary processes *on the atomic scale*.

The process of adsorption - thermodynamical background

Thermodynamical derivation of the so-called isosteric enthalpy of adsorption, q_{st} :

Chemical equilibrium between adsorbate and gas phase leads to a *constant surface concentration* Γ [moles/m²]. Constant Γ is maintained when the fluxes of adsorbing and desorbing particles are equal. We now consider the pressure and temperature dependence of this phase equilibrium. A common procedure is to equate the chemical potentials and their derivatives of the phases involved. Remember that the chemical potential μ is the derivative of the Gibbs energy with respect to the mole number in question, n_i :

$$\mu_i = \left(\frac{dG}{dn_i} \right)_{P,T, \text{ other mole numbers}}$$

In the (dynamical) phase equilibrium, the chemical potentials μ_{ad} and μ_{gas} are equal and remain equal ("persisting" or "ongoing" equilibrium):

$$\mu_{ad} = \mu_{gas} \quad \text{and} \quad d\mu_{ad} = d\mu_{gas} ; \quad \Gamma = n_{ad}/A$$

$$d\mu_{ad} = -S_{ad}dT + V_{ad}dP + \left(\frac{\partial \mu_{ad}}{\partial \Gamma} \right)_{P,T} d\Gamma = d\mu_{gas} = -S_g dT + V_g dP.$$

(small letters denote partial molar quantities)

Rearranging and considering that the term $\left(\frac{\partial \mu_{ad}}{\partial \Gamma}\right)_{p,T} d\Gamma$ gets zero for constant coverage ($d\Gamma=0$) yields the well-known Clausius - Clapeyron equation for the “ongoing” phase equilibrium between gas phase and adsorbate phase(s):

$$\left(\frac{dP}{dT}\right)_\Gamma = \frac{s_g - s_{ad}}{V_g - V_{ad}} = \frac{\Delta S}{\Delta V}$$

Setting $V_{ad} \ll V_g$ and applying the ideal gas equation, i.e., $V_g = \frac{RT}{P}$ yields the relation

$$\frac{1}{P} \left(\frac{dP}{dT}\right)_\Gamma = \frac{s_g - s_{ad}}{RT} . \quad \text{Recalling that the entropy is the “reduced” heat } \Delta s = \frac{\Delta h}{T} \text{ finally}$$

leads to the expression:

$$\frac{1}{P} \left(\frac{dP}{dT}\right)_\Gamma = \frac{h_g - h_{ad}}{RT^2} = \left(\frac{d \ln P}{dT}\right)_\Gamma = \frac{q_{st}}{RT^2}$$

q_{st} is called ***differential isosteric heat of adsorption*** and represents the energy difference between the state of the system before and after the adsorption of a differential amount of particles on that surface. **It can be obtained from equilibrium, i.e., adsorption isotherm measurements.** These considerations apply particularly well for *homogeneous single crystal* surfaces, for which we shall provide examples later. Nevertheless, q_{st} is often coverage-dependent due to lateral particle – particle interactions.

Concept of the adsorption isotherm

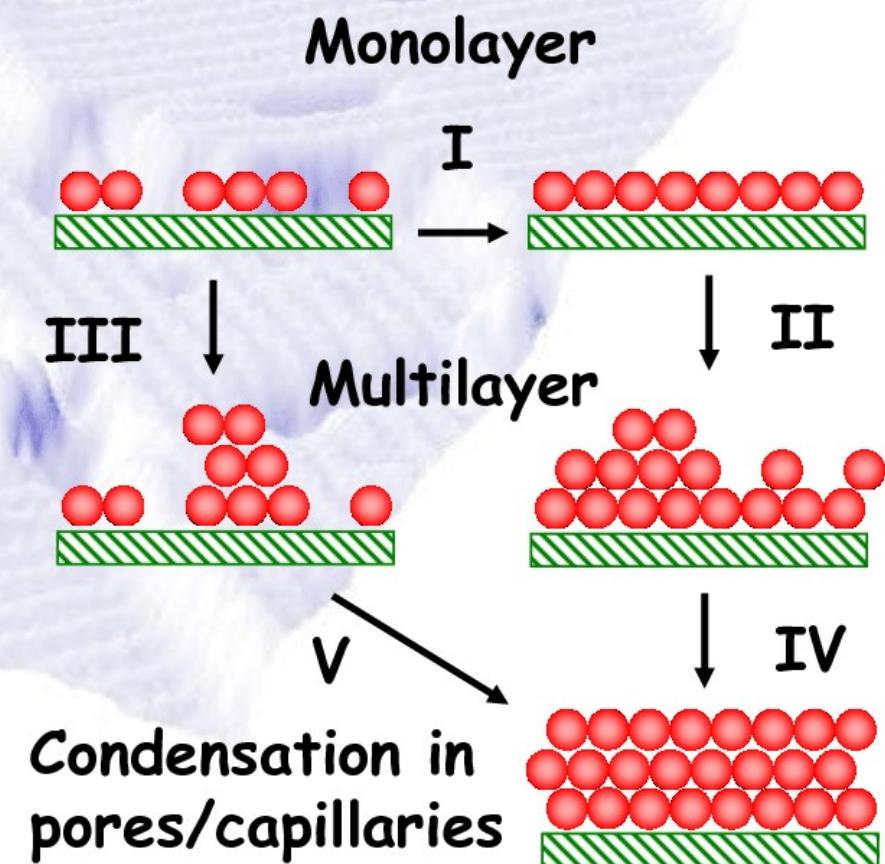
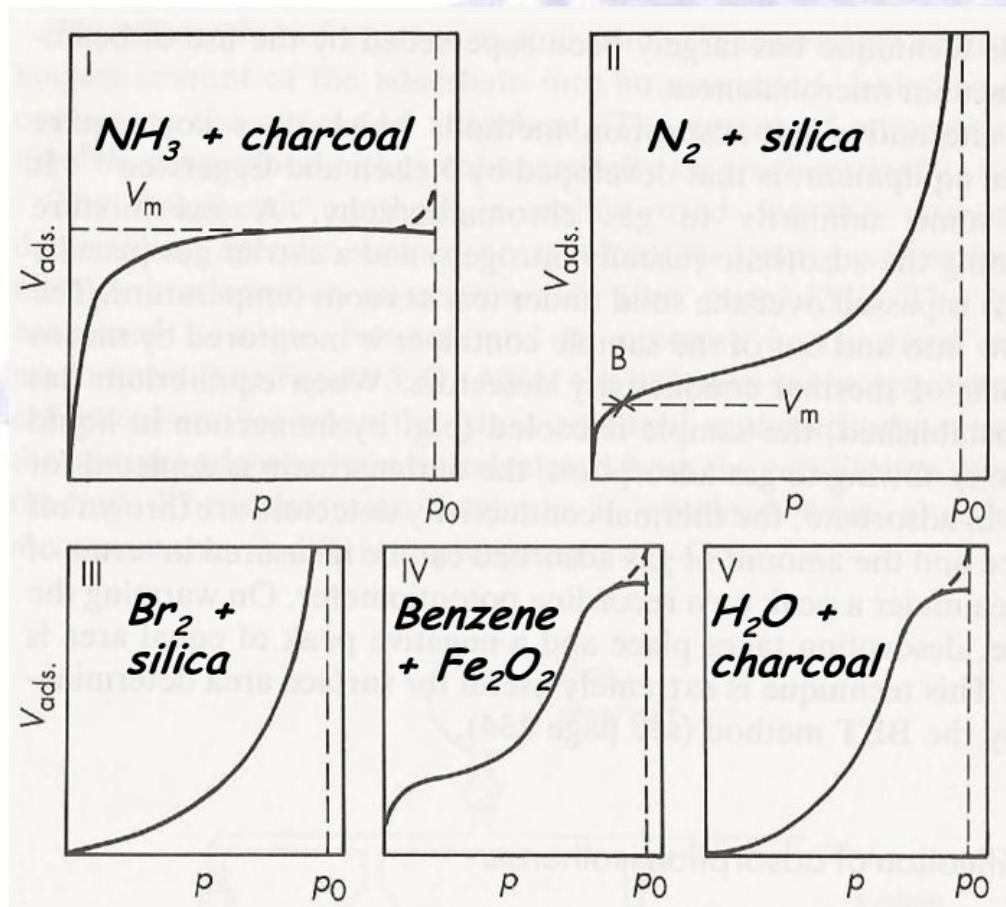
The **adsorption isotherm** displays information of how much material will adsorb for a given set of state variables (pressure P and temperature T when using gases as adsorptives, concentration c and temperature T when dealing with adsorption from solutions). The amount of adsorbed material can be introduced as *surface coverage* Θ , i.e., the fraction of occupied/available sites, or by the *total volume* v_m taken up by the sum of particles adsorbed in the first monolayer.

The adsorption isotherm is one of the most characteristic quantities for an adsorption process. In practice, the **uptake** of adsorptive of a given catalyst material is decisive, since a high uptake usually means a good catalyst efficiency. The respective uptake is often called 'sorption capacity' and characterised by the **sorption** (or adsorption) **isotherm**. The form of the sorption isotherm provides a lot of first-glance information about the chemical and physical properties of the catalyst material and about how the adsorption process proceeds. In principle, various kinds of isotherms can be distinguished, depending on the nature of the catalyst and the kind of interaction.

Adsorption Isotherms

Surface coverage of adsorbate is a function of adsorptive gas or vapour pressure = adsorption isotherm (constant temp)

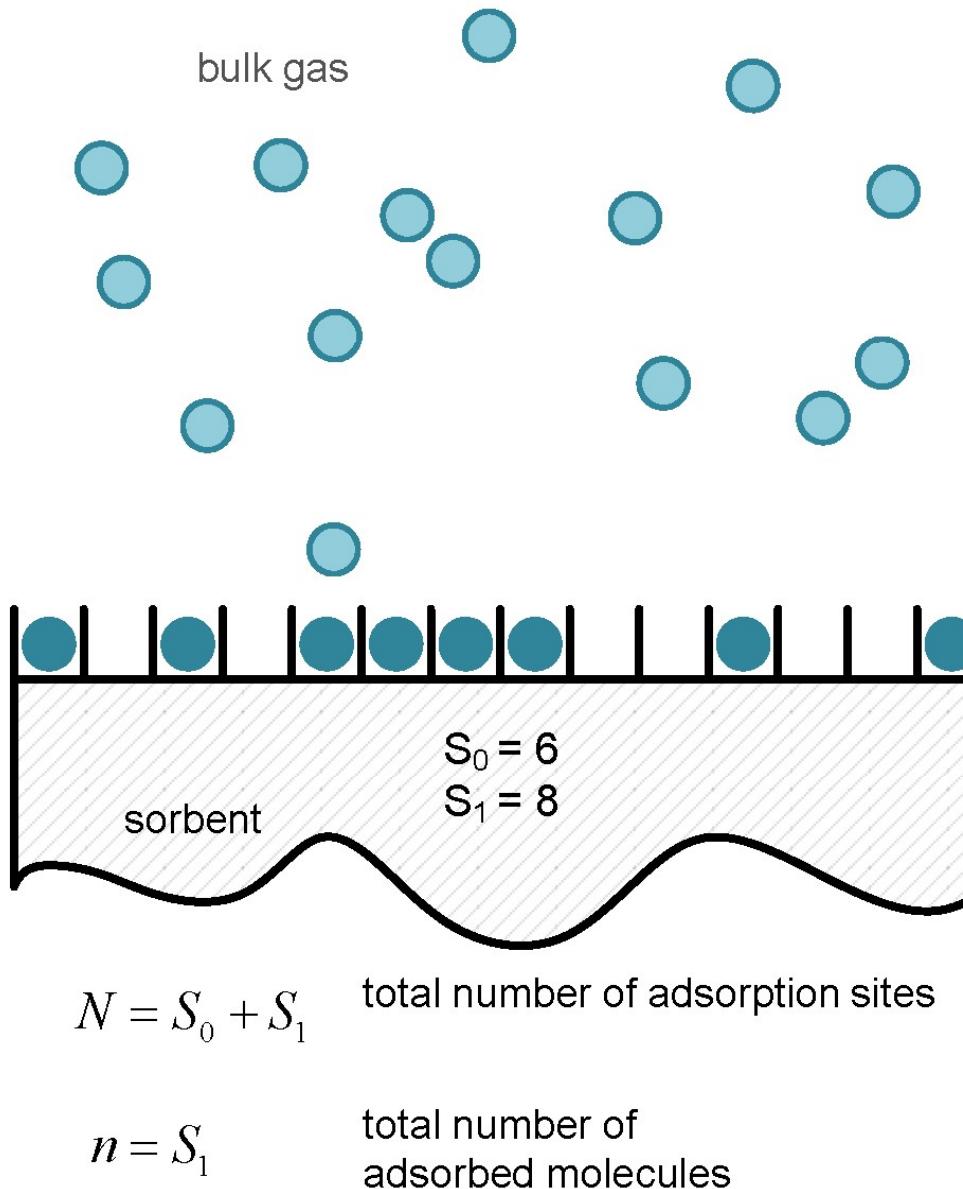
5 types classified by Brunauer in 3 categories



Adsorption Isotherms

- Plot of the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature.
- **Langmuir isotherm** (adsorbed layer one molecule thick)
- **Freundlich isotherm** (Heterogeneous adsorbent surface with different adsorption sites)
- **Brunauer, Emmett and Teller (BET) isotherm** (molecules can be adsorbed more than one layer thick)

Single-layer adsorption: Single component



For sites S_0 :

$$a_o P S_0 \quad \text{death rate of sites } S_0 \text{ (adsorption rate)}$$

$$d_0 S_1 \quad \text{birth rate of sites } S_0 \text{ (desorption rate)}$$

For sites S_j :

$$a_j = 0 \quad \forall j \neq 0 \quad \Rightarrow \quad S_j = 0 \quad \forall j > 1$$

At equilibrium:

$$a_o P S_0 = d_0 S_1$$

$$S_1 = \frac{K}{d_0} P S_0$$

$$S_0 = N - S_1$$

$$\frac{S_1}{N} = \frac{n}{N} = \theta$$

$$\boxed{\theta = K P (1 - \theta)}$$

Langmuir single-component isotherm

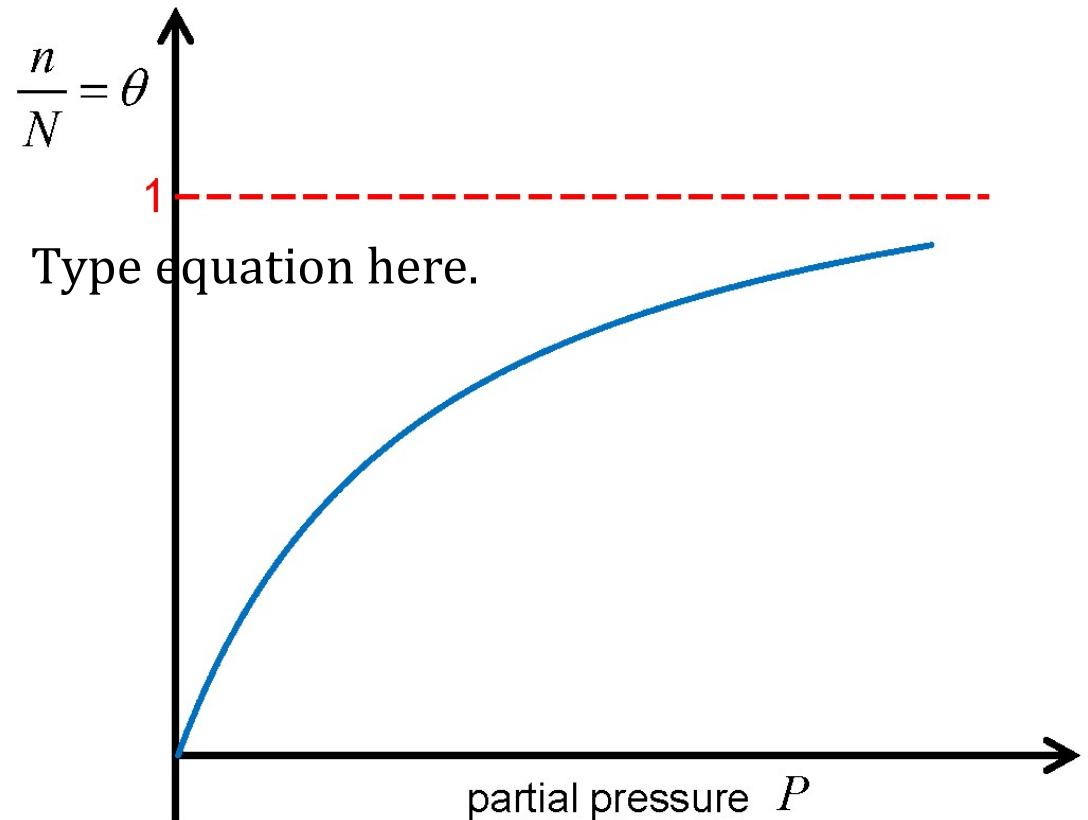
$$\theta = KP(1 - \theta)$$

surface coverage

Langmuir single component isotherm

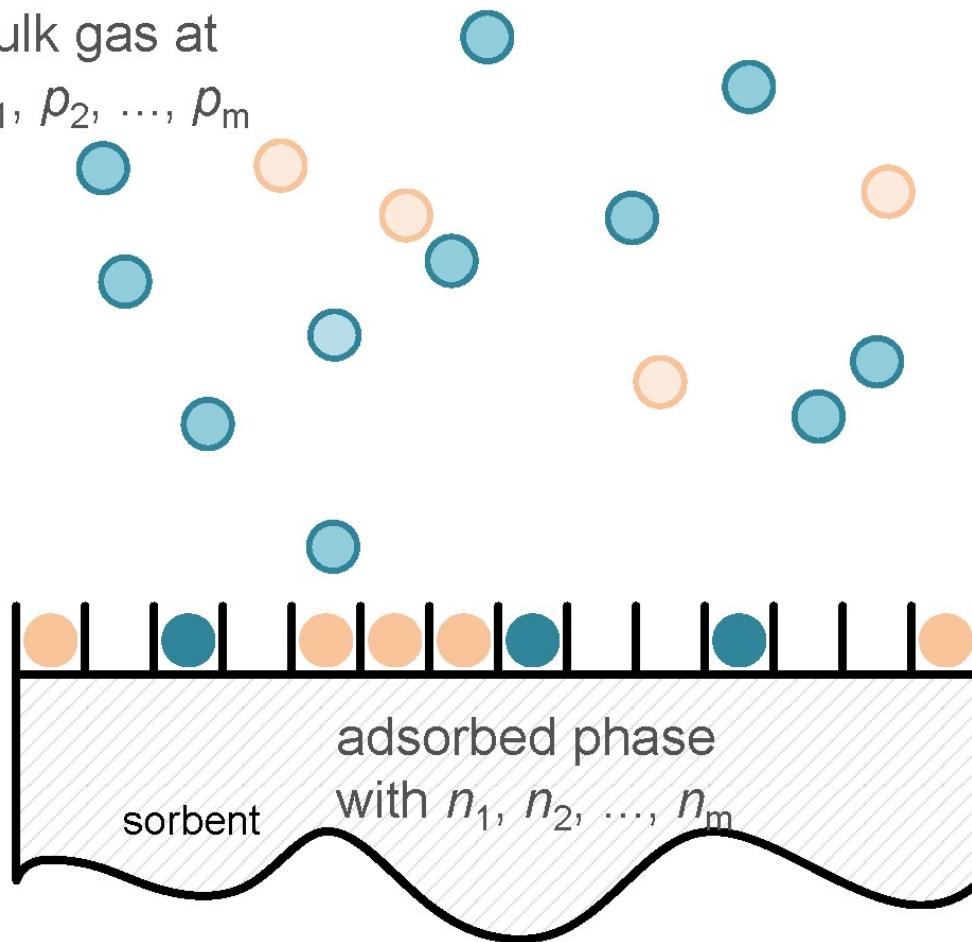
$$\frac{n}{N} = \theta = \frac{KP}{1 + KP}$$

Limit condition: $\lim_{P \rightarrow \infty} \theta = 1$



Competitive single-layer adsorption

bulk gas at
 p_1, p_2, \dots, p_m



Single component: $a_0 P S_0 = d_0 S_1$

$$a_i p_i \left(N - \sum_{j=1}^m n_j \right) = d_i n_i \quad [K_i = a_i/d_i]$$

$$n_i = K_i p_i \left(N - \sum_{j=1}^m n_j \right) \quad \left[\sum_{i=1}^m \{ \} _i \right]$$

$$\sum_{j=1}^m n_j = \left(\sum_{j=1}^m K_j p_j \right) \left(N - \sum_{j=1}^m n_j \right)$$

$$\sum_{j=1}^m n_j = \frac{N \sum_{j=1}^m K_j p_j}{1 + \sum_{j=1}^m K_j p_j} \Rightarrow n_i = \frac{N K_i p_i}{1 + \sum_{j=1}^m K_j p_j}$$

Langmuir
 multi-component
 isotherm

$$\theta_i = \frac{K_i p_i}{1 + \sum_{j=1}^m K_j p_j} \quad \forall i = 1, \dots, m$$

Multi-component Langmuir isotherm

Langmuir
multi-component
isotherm

$$\theta_i = \frac{K_i p_i}{1 + \sum_{j=1}^m K_j p_j} \quad \forall i = 1, \dots, m$$

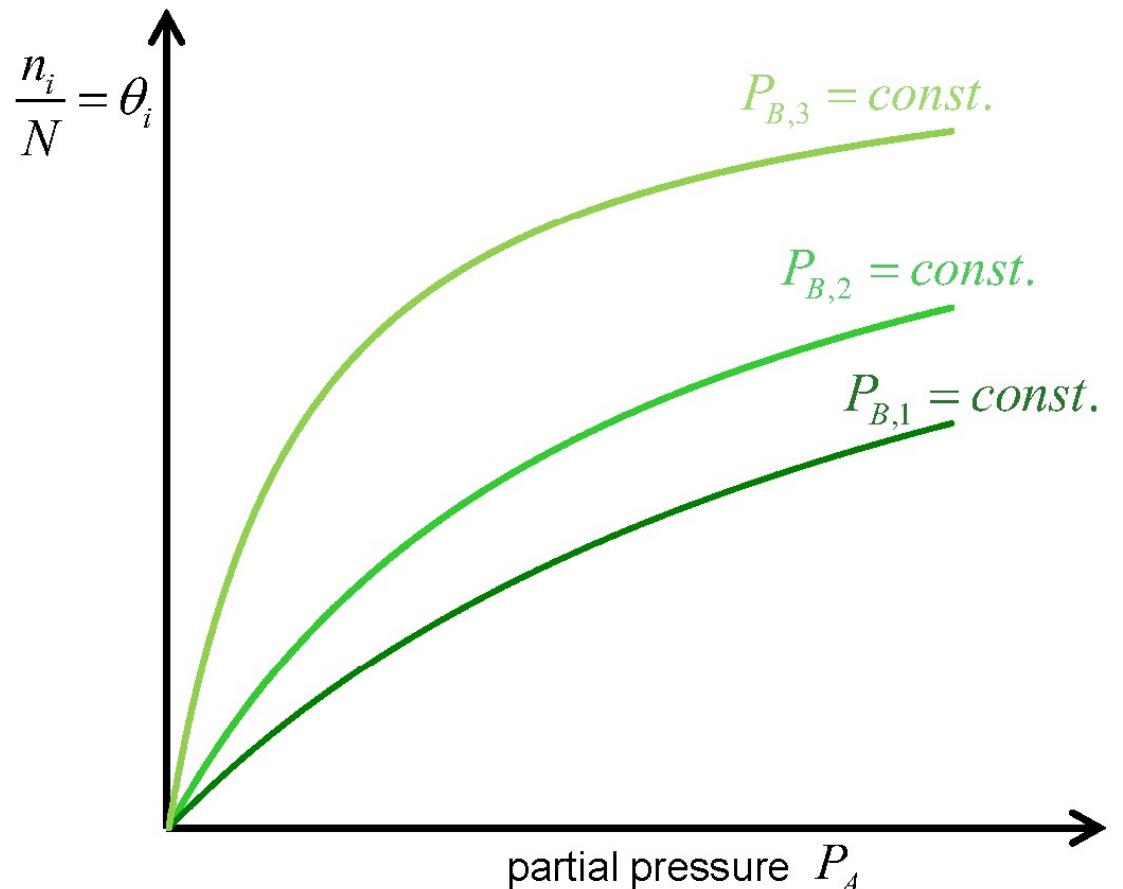
Binary mixture: $A + B$

$$P_{B,1} > P_{B,2} > P_{B,3}$$

$$n_i = \frac{H_i p_i}{1 + K_A p_A + K_B p_B}$$

Selectivity

$$S_{AB} = \frac{n_A/p_A}{n_B/p_B} = \frac{H_A}{H_B} > 1$$



Freundlich Isotherm

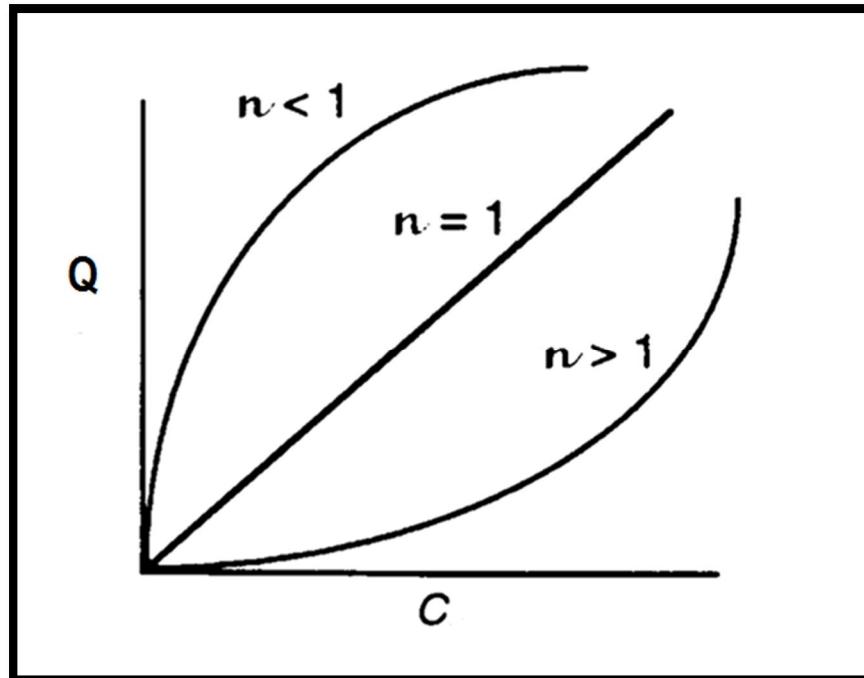
- Freundlich and Küster (1909)

- Relation:

$$Q = K_G p^n$$

$$Q = K_L c^n$$

- Limitation: Fails at high pressures



Q - Mass of adsorbate / mass of adsorbent
 p - equilibrium pressure of adsorbate
 c - equilibrium con. Of adsorbate in solution
 K, n - constants

BET Isotherm

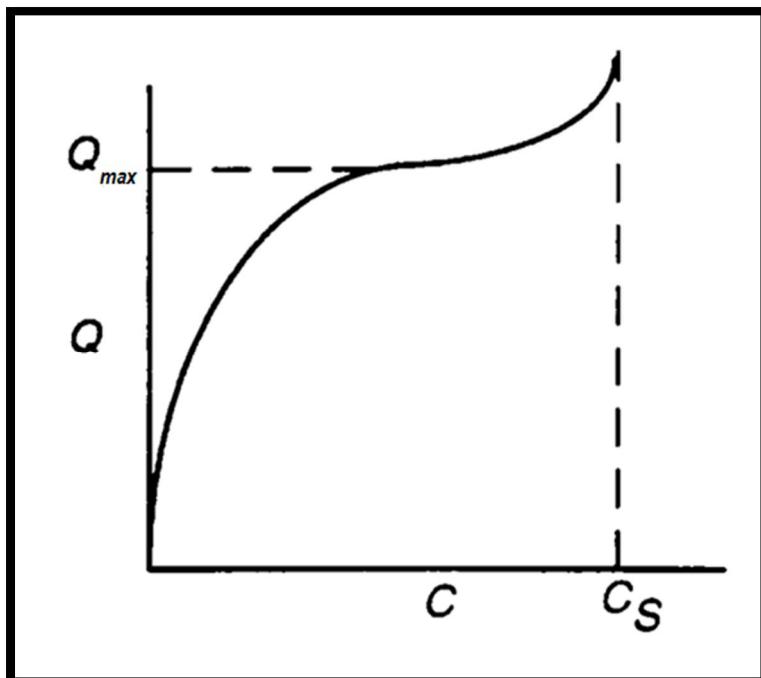
- Stephen Brunauer, Paul Hugh Emmett and Edward Teller (1938)
- Assumptions:

Multilayer

Equal Energy

No Transmigration

Langmuir to each layer



$$Q = \frac{Q_{max} K_B c}{(c_s - c) \left\{ 1 + (K_B - 1) \left(\frac{c}{c_s} \right) \right\}}$$

c_s - saturation (solubility limit)

concentration of the solute

K_B - a parameter related to the binding intensity for all layers.

Equilibrium modelling

Why?

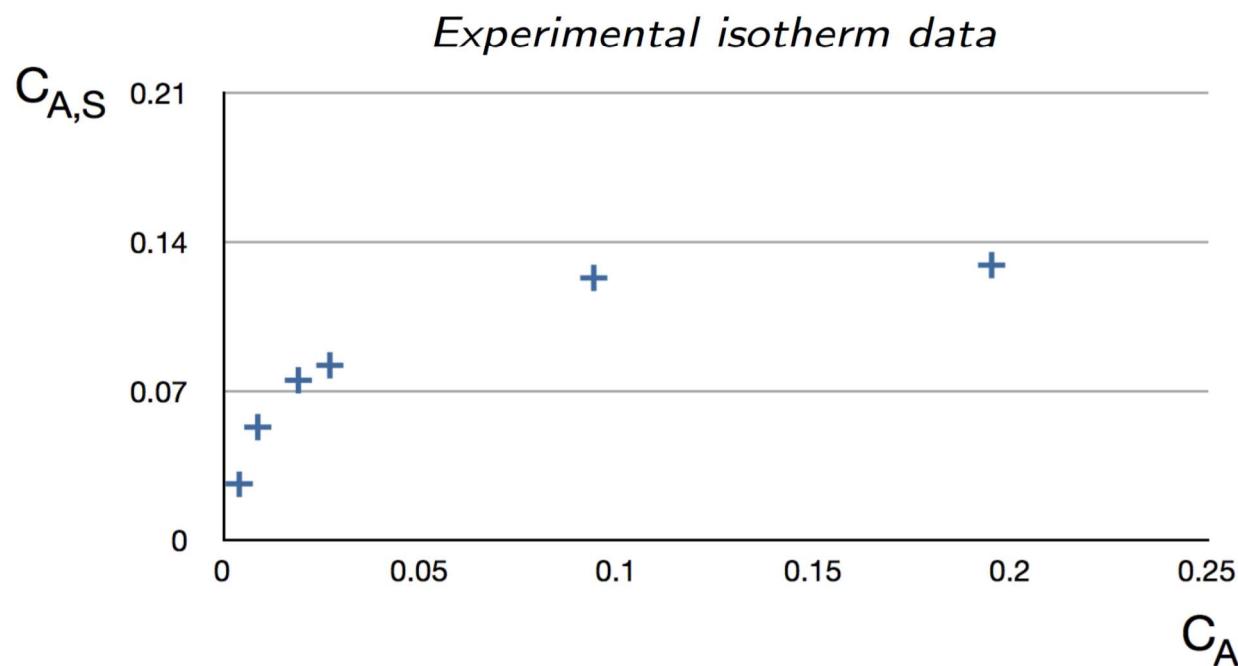
We ultimately would like to determine **how much adsorbent is required** to remove a given amount of adsorbate (e.g. impurity); particularly in batch processes.

For now, assume we are only limited by equilibrium [we'll get there, we don't mind *how long* (due to kinetics of diffusion and mass transfer resistance) it takes to get there]

- ▶ Derive/Postulate a model relating bulk concentration to surface concentration of adsorbate
- ▶ We call these equilibrium equations: “isotherms”
- ▶ **Isotherm**: relates amount of adsorbate on adsorbent ($C_{A,S}$) at different concentrations of adsorbate in the bulk (C_A), but at a fixed temperature.

Further questions to try

2.5 m³ of wastewater solution with 0.25 kg phenol/m³ is mixed with 3.0 kg granular activated carbon until equilibrium is reached. Use the following isotherm, determined from lab values, to calculate the final equilibrium values of phenol extracted and percent recovery. Show the operating point on the isotherm. Units of C_A are [kg per m³] and $C_{A,S}$ is in [kg solute per kg of activated carbon].



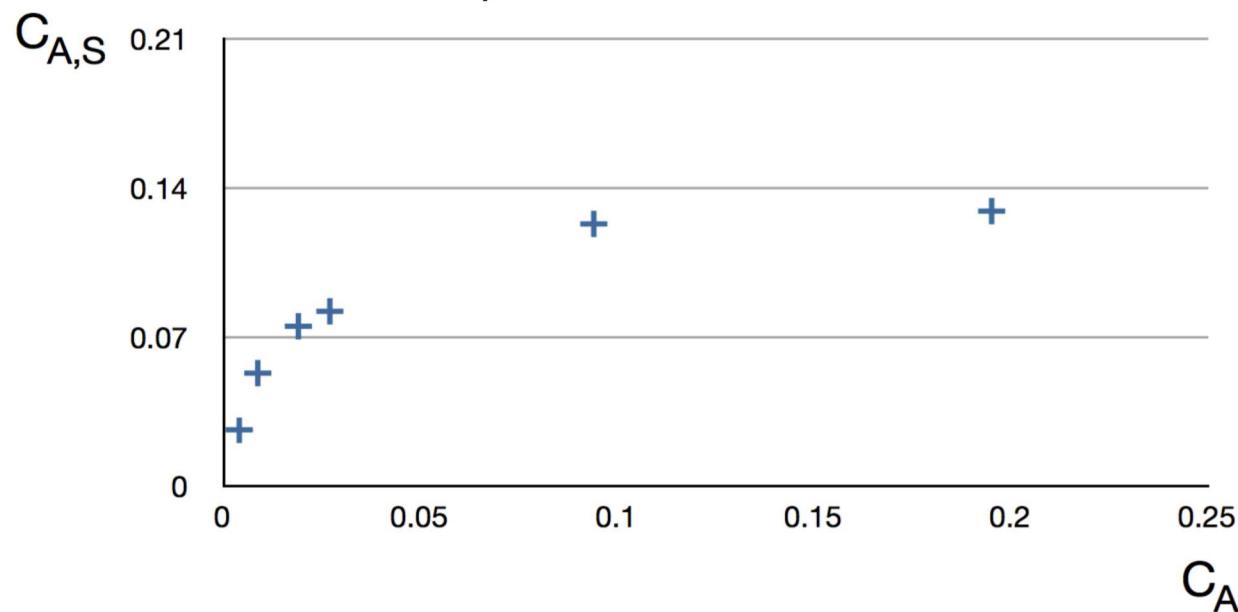
$$C_{A,S} = \frac{0.145C_A}{0.0174 + C_A}$$

Further questions to try

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[Ans: $C_A \approx 0.10$ kg per m³, $C_{A,S} \approx 0.12$ kg/kg, recovery = 58%]

Experimental isotherm data



$$C_{A,S} = \frac{0.145C_A}{0.0174 + C_A}$$

Adsorption kinetics models

Kinetic Model	Nonlinear Model	Linearized Form
Zero-order	$\frac{dq_t}{dt} = c_o$	$q_t = c_0 t + q_o$
First-order	$\frac{dq_t}{dt} = c_1 q_t$	$\log q_t = \log q_o + \frac{c_1}{2.303} t$
Second-order	$\frac{dq_t}{dt} = c_2 q_t^2$	$\frac{-1}{q_t} = c_2 t + \left(\frac{-1}{q_0}\right)$
Pseudo first-order	$\frac{dq_t}{dt} = c_3(q_e - q_t)$	$\log(q_e - q_t) = \log q_e - \frac{c_3}{2.303} t$
Pseudo second-order	$\frac{dq_t}{dt} = c_4(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{c_4 q_e^2} + \frac{1}{q_e} t$
Elovich	$\frac{dq_t}{dt} = \alpha e^{-\beta t}$	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$

q_t (mg g⁻¹) is the amount of metal adsorbed at time t (min); c_o (mg g⁻¹ min⁻¹) is the zero-order rate constant; c_1 (mg g⁻¹ min⁻¹) is the first-order rate constant; c_2 (g mg⁻¹ min⁻¹) is the second-order rate constant; c_3 (mg g⁻¹ min⁻¹) is the pseudo first-order rate constant; c_4 (g mg⁻¹ min⁻¹) is the pseudo second-order rate constant; α (mg g⁻¹ min⁻¹) is the initial adsorption rate; β (g mg⁻¹) is the extent of surface coverage and activation energy for chemisorption

Adsorption diffusion models

Typically for a liquid/solid adsorption: film diffusion, intra-particle diffusion, and mass action are the key mass transport. For physical adsorption, mass action is a very rapid process and can be negligible for kinetic study. Thus, the kinetic process of adsorption is always controlled by liquid film diffusion or intra-particle diffusion, i.e., one of the processes should be the rate limiting step.

Linear driving force rate law: the rate of solute accumulation in the solid phase is equal to that of solute transfer across the liquid film according to the mass balance law.

The rate of solute accumulation in a solid particle is $V_p \left(\frac{\partial \bar{q}}{\partial t} \right)$ where \bar{q} represents the average solute concentration in the solid, and V_p the volume of the particle. Meanwhile the rate of solute transfer across the liquid film is proportional to the surface area of the particle A_s and the concentration driving force ($C - C_i$). Therefore, it equals to $k_f A_s (C - C_i)$, where k_f represents the film mass transfer coefficient

$$V_p \left(\frac{\partial \bar{q}}{\partial t} \right) = k_f A_s (C - C_i)$$

Intra-particle diffusion model

Homogeneous solid diffusion model

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left[r^2 \cdot \frac{\partial q}{\partial r} \right]$$

Soln: $\frac{q}{q_s} =$

The average value of q in the sphere at any time t

$$\bar{q} = \frac{3}{R^3} \int_0^R q(r) r^2 dr$$

$\therefore \frac{\bar{q}}{q_\infty} =$

avg. conc. in the solid @ $t \rightarrow \infty$

Intra-particle diffusion model

Homogeneous solid diffusion model

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left[r^2 \cdot \frac{\partial q}{\partial r} \right]$$

Soln: $\frac{q}{q_s} = 1 + \frac{2R}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{R} \exp \left[-\frac{D_s n^2 \pi^2 t}{R^2} \right]$

The average value of q in the sphere at any time t

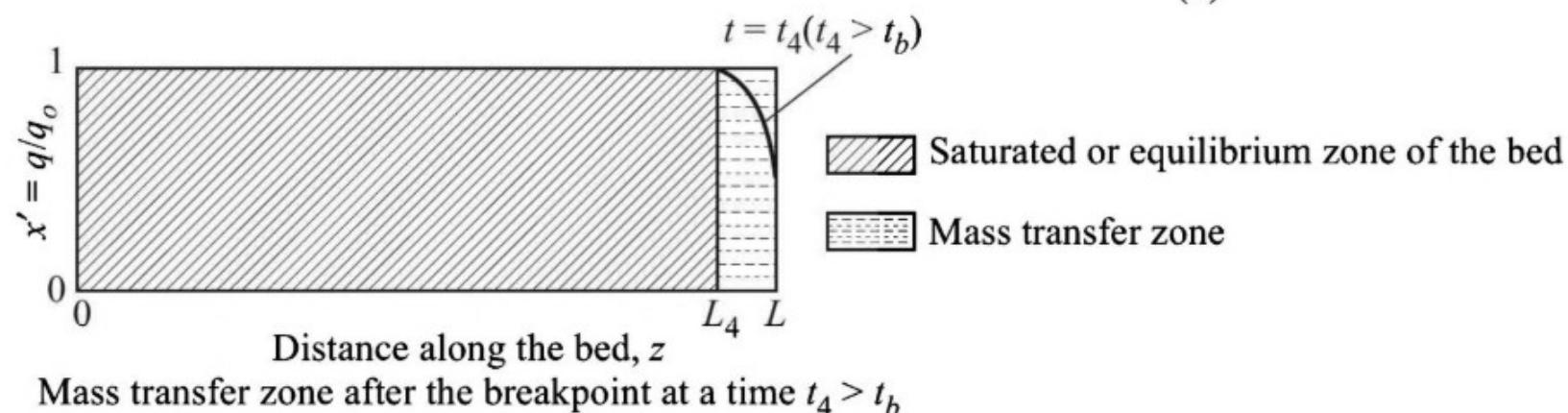
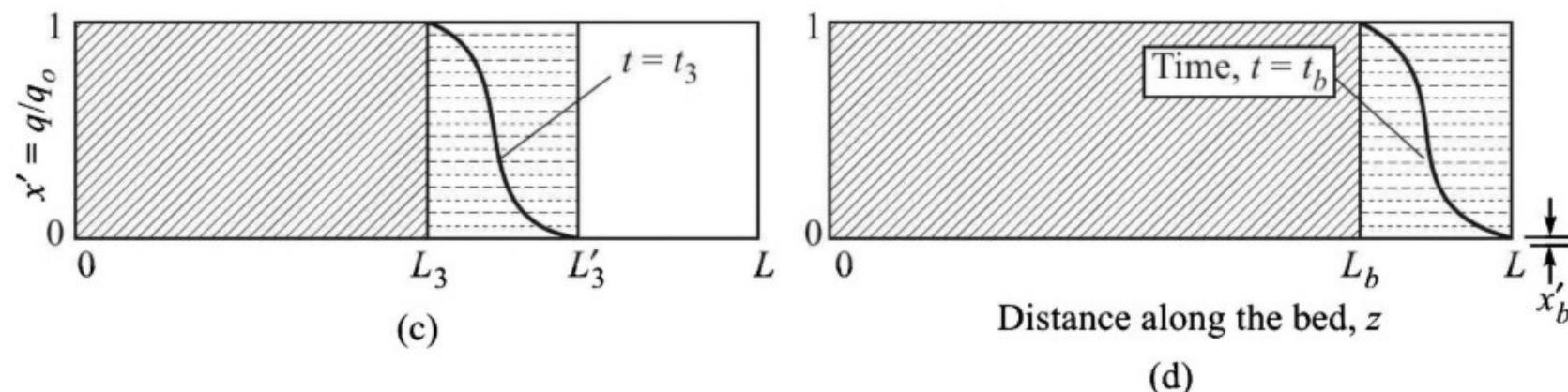
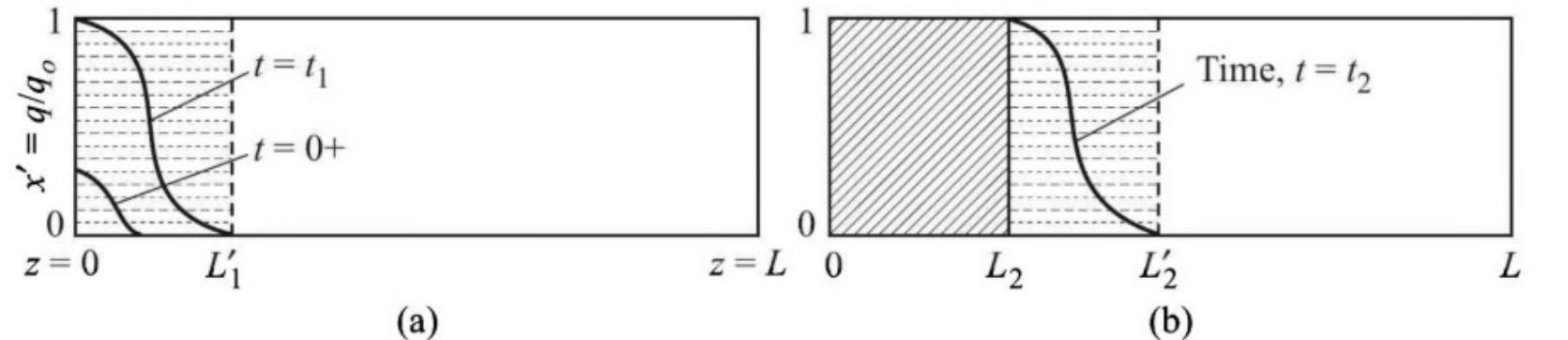
$$\bar{q} = \frac{3}{R^3} \int_0^R q(r) r^2 dr$$

$$\therefore \frac{\bar{q}}{q_s} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[-\frac{D_s n^2 \pi^2 t}{R^2} \right]$$

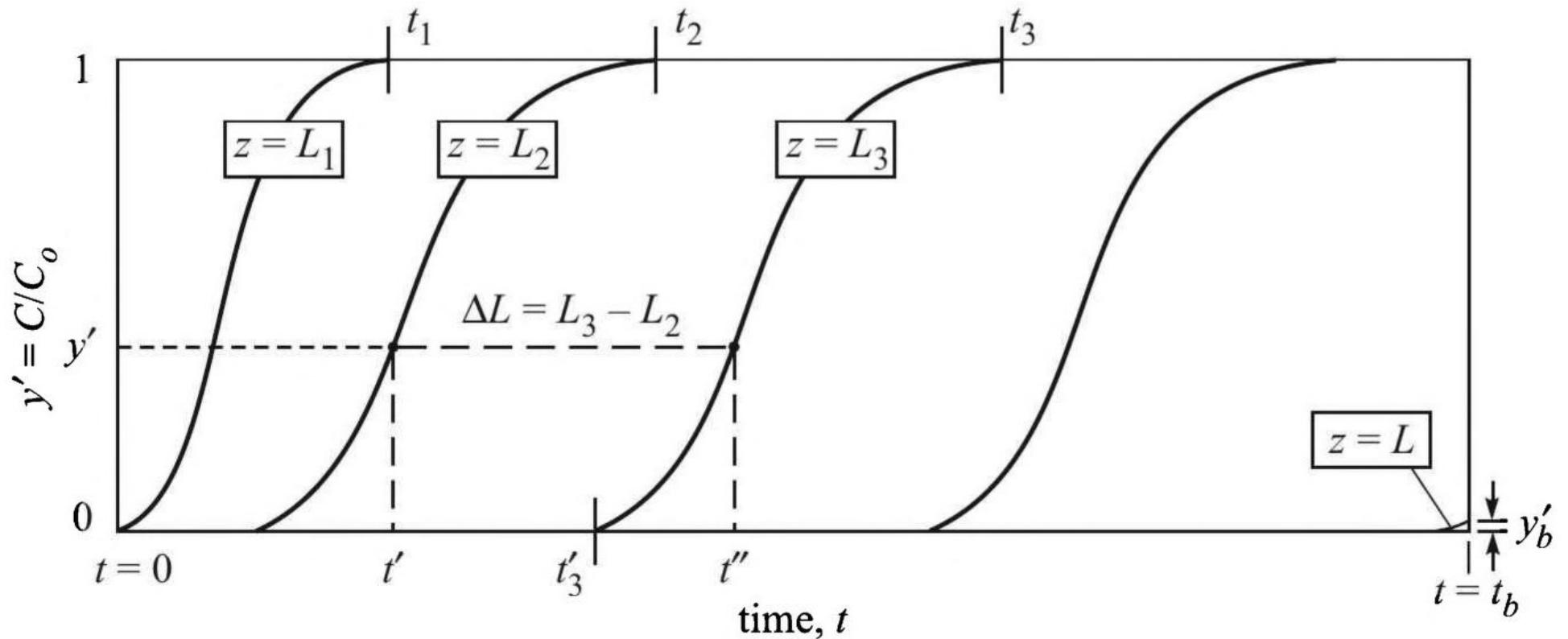
avg. conc. in the solid @ $t \rightarrow \infty$

Adsorption dynamics: Fixed bed adsorber

Mass transfer zone

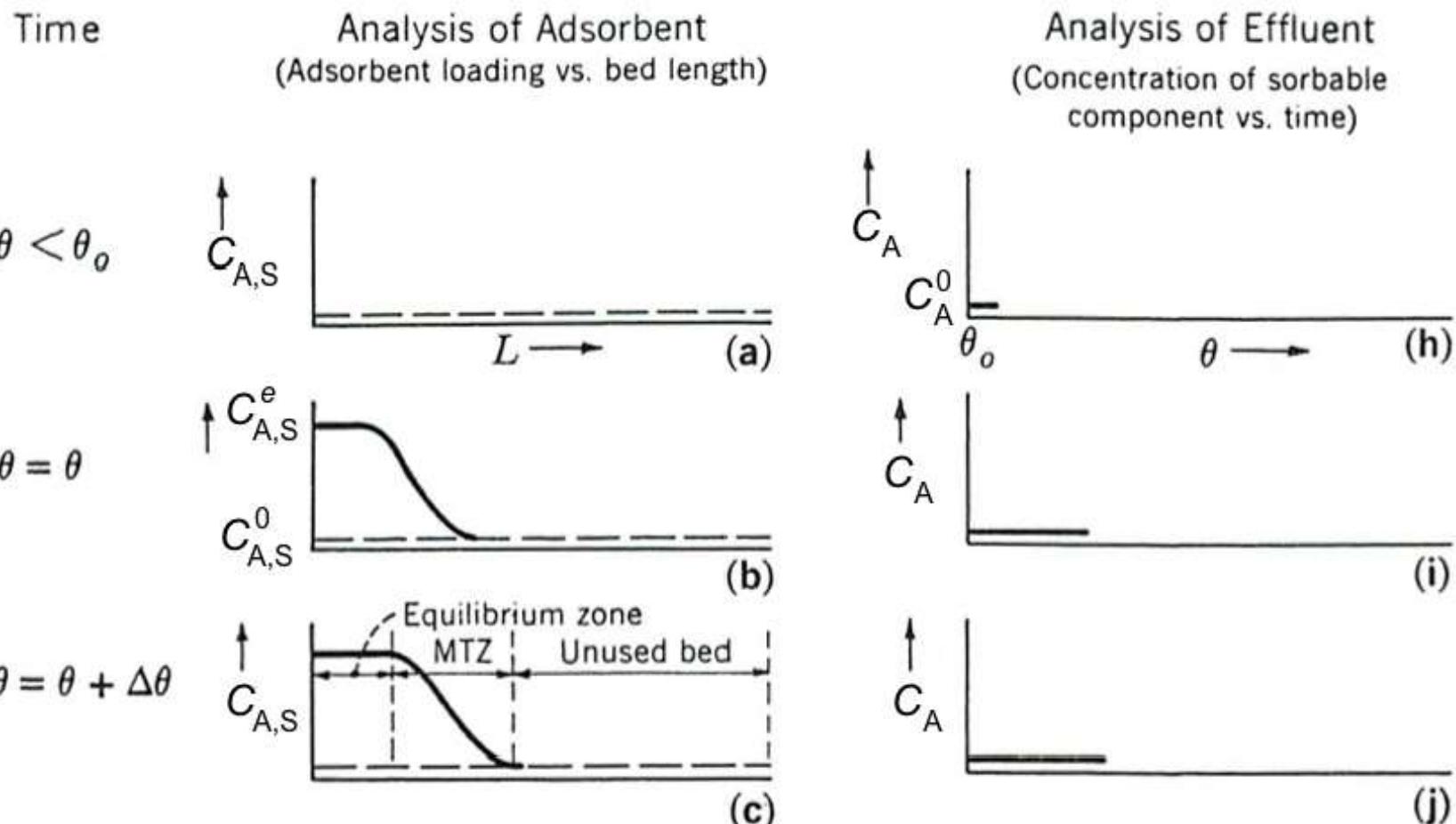
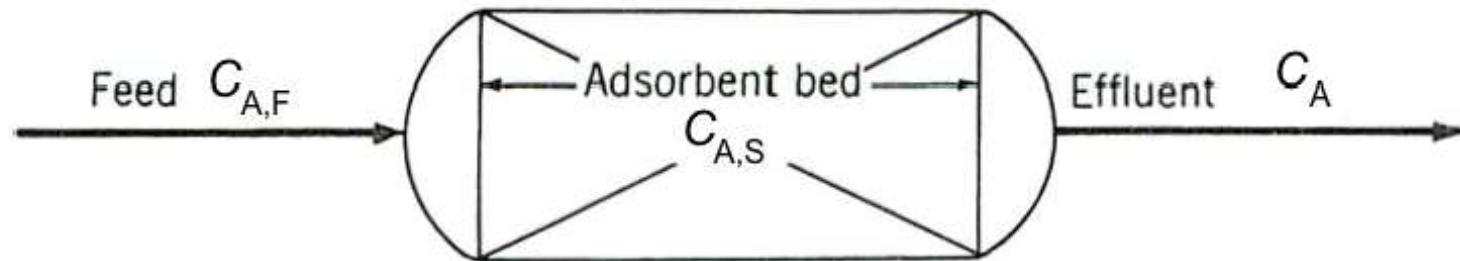


Breakthrough



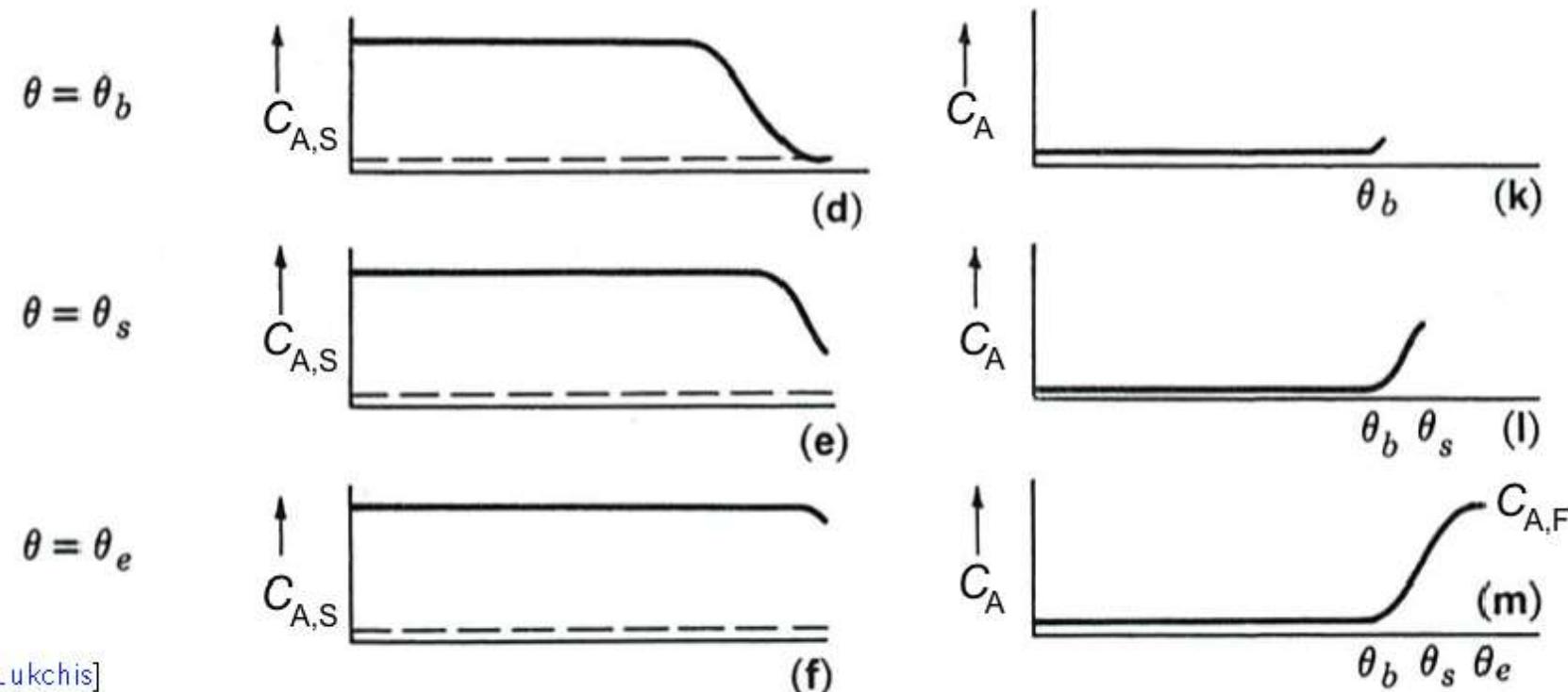
Concentration history of the solute in the gas at different axial positions

Understanding adsorption in packed beds (1 of 2)



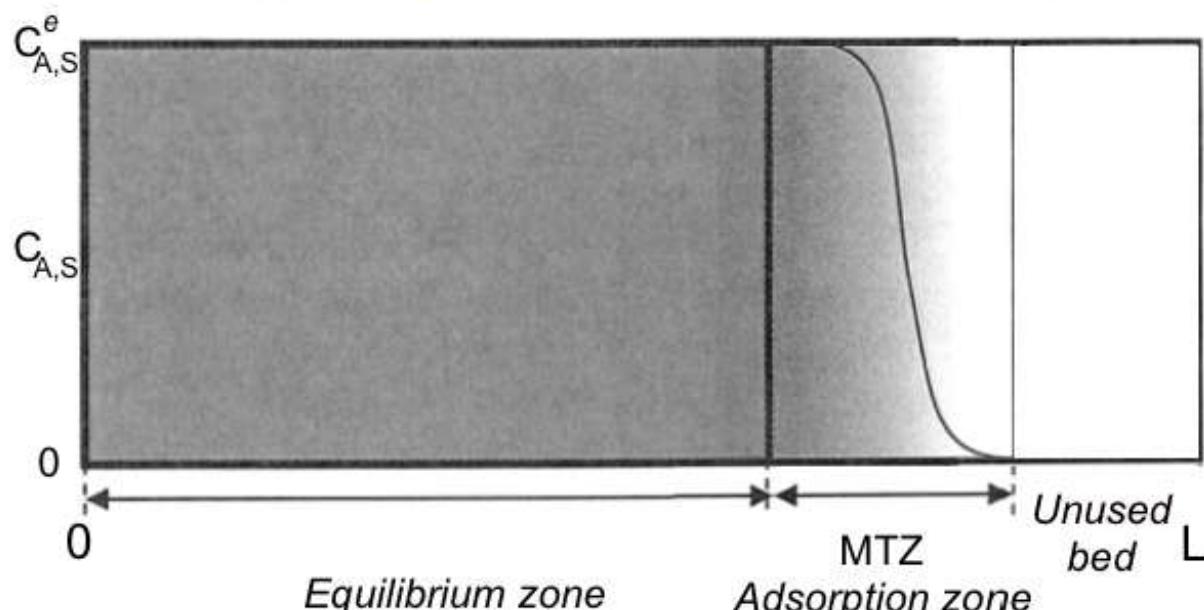
L = length; θ = time; θ_0 = start-up time on a regenerated bed

Understanding adsorption in packed beds (2 of 2)



- ▶ $C_{A,S}$ = concentration of adsorbate on adsorbent
- ▶ $C_{A,S}^e$ = concentration at equilibrium on the adsorbent (**equil loading**)
- ▶ $C_{A,S}^0$ = concentration on the regenerated adsorbent at time 0
- ▶ θ_b = breakthrough time: “*time to stop using the packed bed!*”; usually when $C_A = 0.05C_{A,F}$
- ▶ θ_e = the bed at equilibrium time; packed bed is completely used
- ▶ $C_{A,S}$ values are not easy measured; outlet concentration C_A is easy

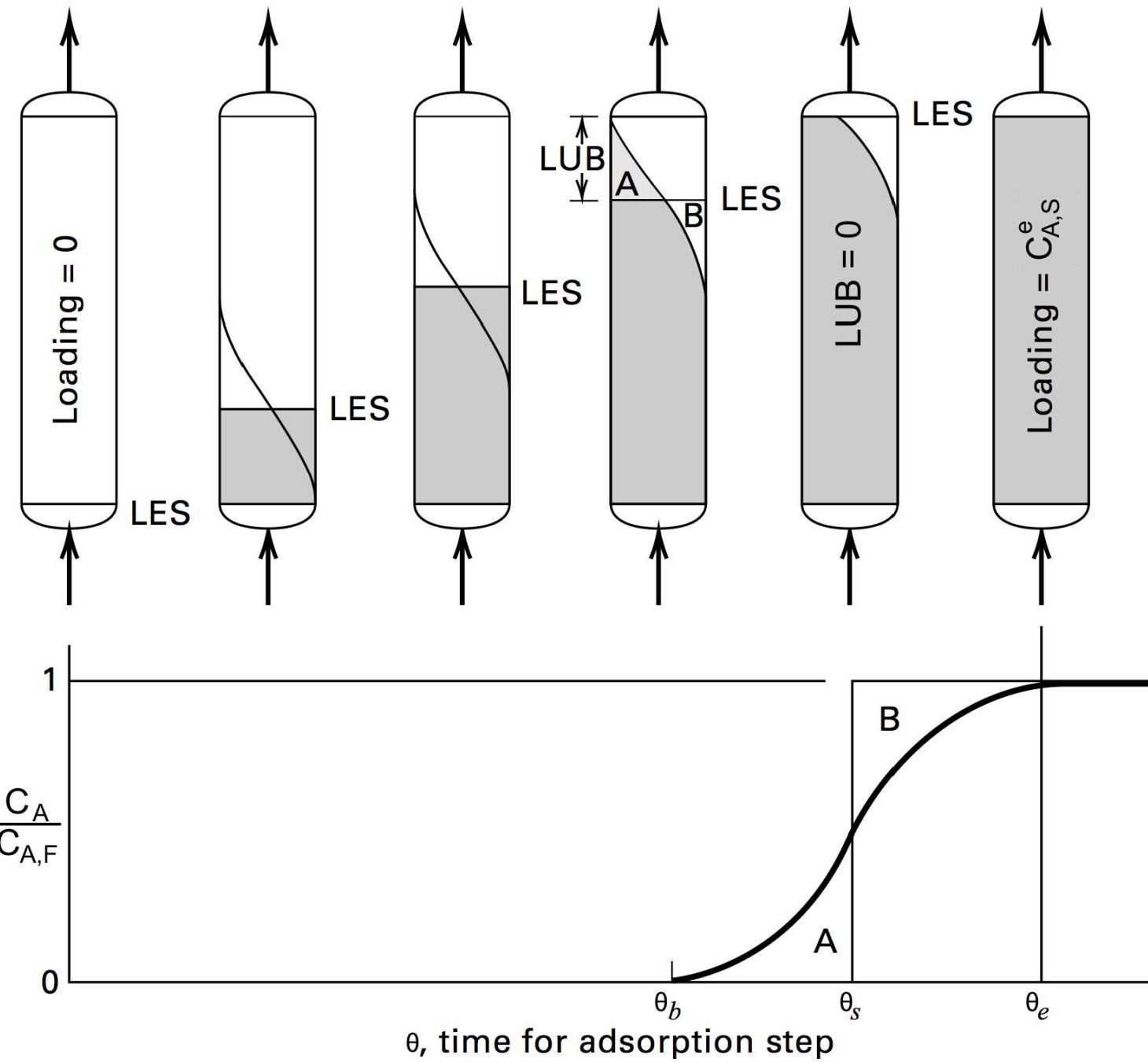
Bed concentration just prior to breakthrough



[Ghosh (adapted), p144]

- ▶ **MTZ:** mass transfer zone is where adsorption takes place.
- ▶ It is S-shaped: indicates there is mass-transfer resistance and axial dispersion and mixing. Contrast to the ideal shape: is a perfectly vertical line moving through the bed
- ▶ **Equilibrium zone:** this is where the isotherm applies!
- ▶ **Breakthrough:** arbitrarily **defined as time** when either (a) the lower limit of adsorbate detection, or (b) the maximum allowable adsorbate in effluent leaves the bed. Usually around 1 to 5% of $C_{A,F}^e$.

Figures to help with the next example

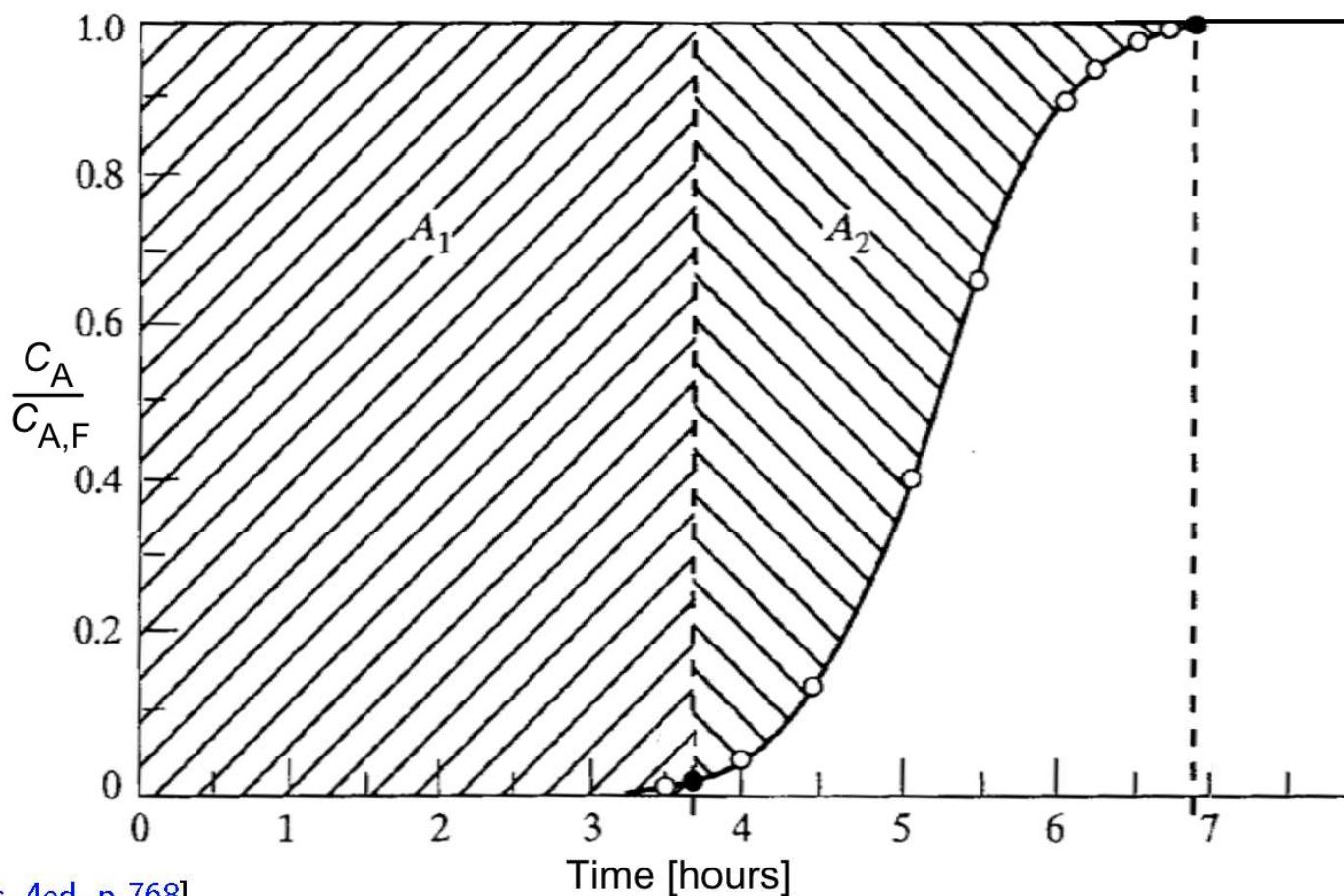


Terminology

- ▶ **LES** = length of equilibrium section (increases as bed is used)
- ▶ **LUB** = length of unused bed (decreases as bed is used up)
- ▶ L = total bed length = LES + LUB
- ▶ No data available: use MTZ distance of 4ft

Example (and some new theory applied)

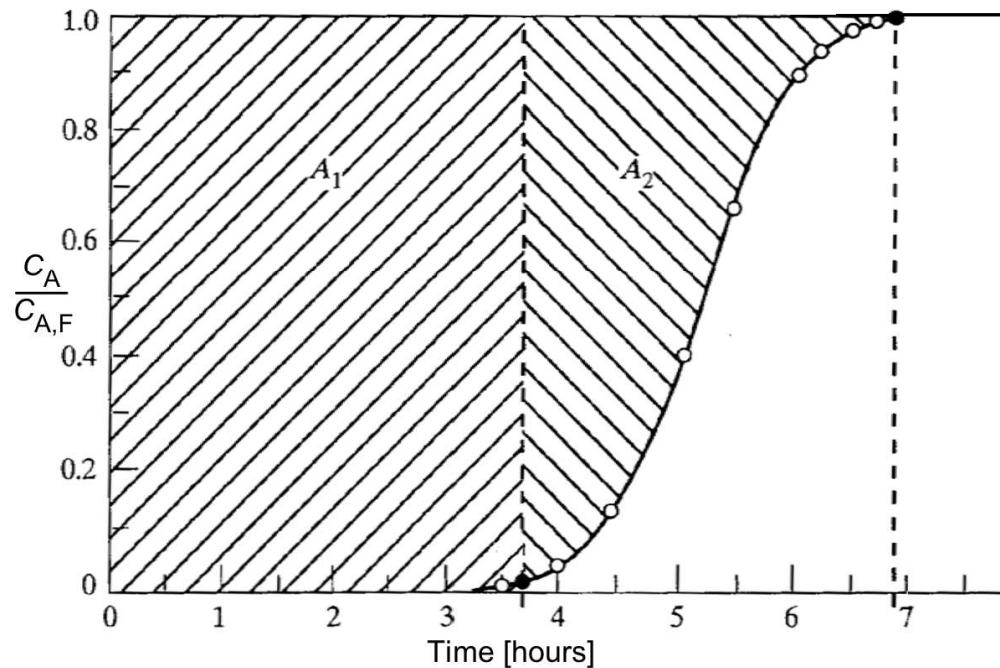
An adsorbate in vapour is adsorbed in an experimental packed bed. The inlet contains $C_{A,F} = 600$ ppm of adsorbate. Data measuring the outlet concentration over time from the bed are plotted below:



[Geankoplis, 4ed, p 768]

Example

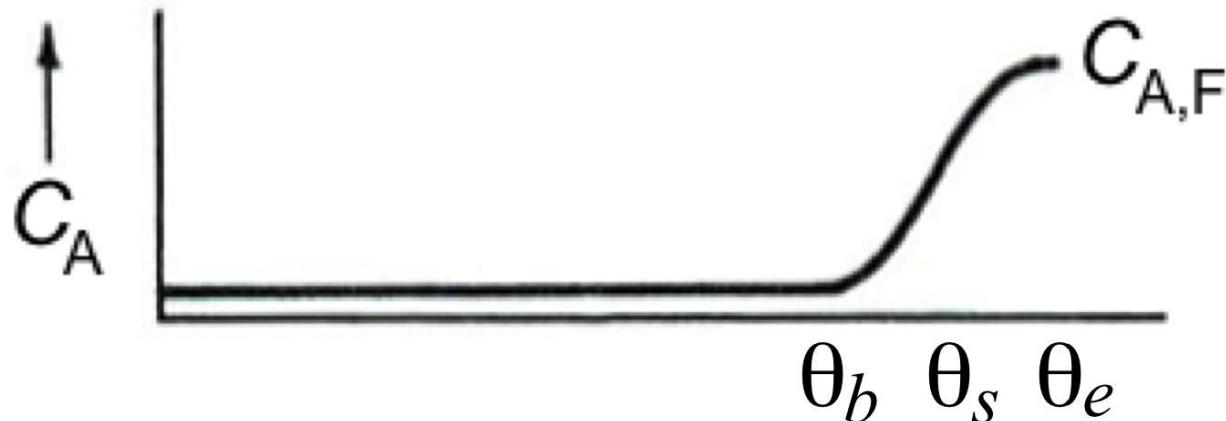
1. Determine the breakthrough time, θ_b . [Ans: 3.65 hours]
2. What would be the usable capacity of the bed at time θ_b if we had an ideal waveform (no mass transfer resistance)? [Ans: the fractional area of $A_1 = 3.65 / 6.9 = 53\%$]
 - ▶ Note plot area units = “total time”, since “height” of y-axis = 1.0
 - ▶ Note: (area up to θ_b) $\approx \theta_b$ when using a normalized y-axis



3. How long does it take to reach this ideal capacity? ≈ 3.65 hours
Ignore the tiny part missing from the integrated area.

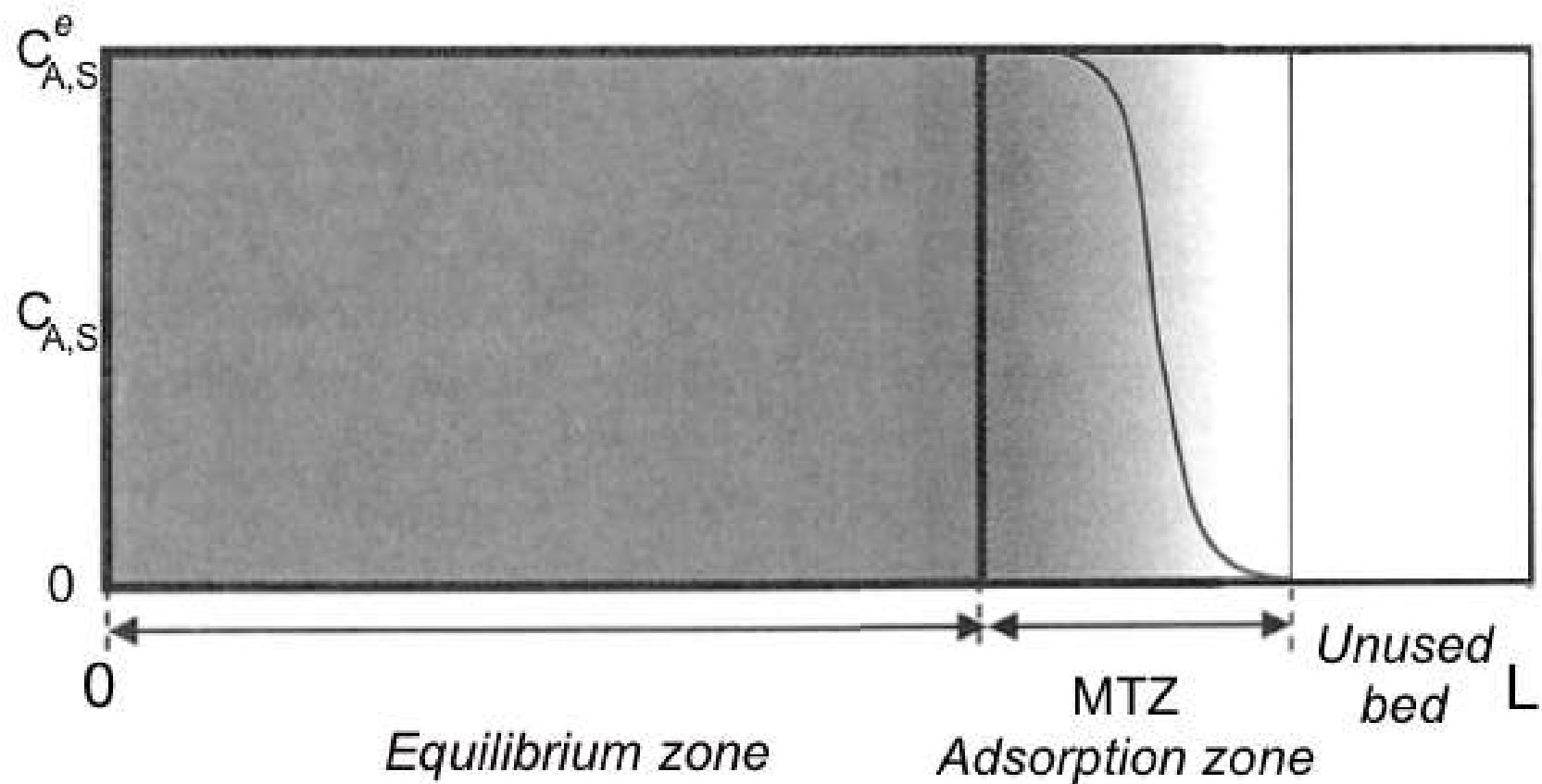
Example

4. What actual fraction of the bed's capacity is used at θ_b ?



- ▶ The actual capacity used is the total shaded area = $A_1 + A_2$
- ▶ This is called the **stoichiometric capacity** of the bed
- ▶ Ideally, if there were no mass transfer resistance (i.e. spread in the breakthrough curve), then the
- ▶ **stoichiometric time**, θ_s , is defined as **time taken for this *actual capacity* to be used**
- ▶ θ_s is the point that breaks the MTZ into equal areas: in this case, A_2 vs the unshaded area in previous diagram
- ▶ $\theta_s = \int_0^\infty \left(1 - \frac{C_A}{C_{A,F}}\right) dt = \text{shaded area} = A_1 + A_2 = 3.65 + 1.55 = 5.20 \text{ hrs}$
- ▶ So actual bed fraction used at θ_b is $\frac{5.2}{6.9} = 0.75 \sim 75\%$

Figures to help with the example



5. If the lab-scale bed was originally 14cm long, what equivalent “length” is unused at time θ_b ?
 - ▶ intuitively: $(1 - 0.75) \times 14 \text{ cm} = 3.5 \text{ cm}$
 - ▶ LUB = length of unused bed = 3.5 cm
 - ▶ LES = length of equilibrium section = the used up part = $14.0 - 3.5 = 10.5 \text{ cm}$

Example

6. If we wanted a break-point time of $\theta_b = 7.5$ hours instead, how much longer should the bed be (keeping the diameter and flow profile fixed)?

	Current	Desired
LES	$0.75 \times 14 \text{ cm} = 10.5 \text{ cm}$	21.6cm
LUB	$0.25 \times 14 \text{ cm} = 3.5 \text{ cm}$	3.5cm
Total	14cm	25.1cm

- Ratio LES lengths to breakthrough times: $\frac{\text{LES}^{\text{des}}}{\text{LES}^{\text{curr}}} = \frac{\theta_b^{\text{des}}}{\theta_b^{\text{curr}}}$
- Length to get to breakthrough in 7.5 hours = $\text{LES}^{\text{des}} = 21.6 \text{ cm}$
- We have to add on the length of the unused bed = 3.5 cm from before (same diameter, same flow profile!)
- So new bed length = $\text{LES} + \text{LUB} = 21.6 + 3.5 = 25.1 \text{ cm}$
- LUB is the same length, provided all other conditions are the same
- Then fraction actually used = $\frac{21.6}{24.5} = 0.88$ (compared to 0.75)

Bed mass balance

Amount of material loaded into the bed up to θ_b in LES

$$Q_F \ C_{A,F} \ \theta_b = C_{A,S}^e \ \rho_B \ A \ L_{LES}$$

Q_F	Feed flow rate	$\left[\frac{m^3}{\text{second}} \right]$
$C_{A,F}$	Inlet concentration	$\left[\frac{\text{kg solute}}{m^3 \text{ fluid}} \right]$
θ_b	Breakthrough time	[second]
$C_{A,S}^e$	Eqbm adsorbed solute conc ⁿ	$\left[\frac{\text{kg solute}}{\text{kg adsorbent}} \right]$
ρ_B	Adsorbent's bulk density	$\left[\frac{\text{kg adsorbent charged}}{m^3 \text{ of occupied space}} \right]$
$A L_{LES}$	Bed volume = area \times LES length	$\left[m^3 \text{ of occupied space} \right]$

Add on LUB; determine volume adsorbent required = $A(L_{LES} + L_{LUB})$.

Take porosity into account when calculating mass of adsorbent from the occupied volume.

Another question

Trimethylethylene (TME) is being removed from an aqueous chemical plant waste stream on a *continuous basis* (this is not a batch system). A bench scale system indicates that the adsorbent follows a Langmuir adsorption isotherm as:

$$C_{A,S} = \frac{0.05 C_A}{32.1 + C_A}$$

where $C_{A,S}$ has units of [grams/grams], and the constant has units of 32.1 ppm. In a tank we have an inlet flow of TME solution at 10L/min with density of 1000 kg.m^{-3} . The TME enters at 100 ppm (parts per million, mass solute per 10^6 mass solution) in the feed. The impurity is not detectable below 1 ppm concentrations. The tank contains 15 kg of initially fresh adsorbent which is retained in the tank. We wish to know:

1. How much TME is adsorbed when the breakthrough concentration reaches 1 ppm?
2. How long it will take to reach this detectable outlet concentration?

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1. How much TME is adsorbed when the breakthrough concentration reaches 1 ppm? [Ans: 22.66 g]
2. How long it will take to reach this detectable outlet concentration? [22.6 minutes]

Breakthrough modelling in fixed bed adsorption

Thomas model:

Assumes the second-order reversible reaction kinetics and the Langmuir isotherm. Theoretically, it is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small

$$\ln\left(\frac{C_F}{C} - 1\right) = \frac{k_{\text{Th}} q_F m}{Q} - k_{\text{Th}} C_F t$$

This equation is applied when $\ln(C_F/C) - 1$ vs. t is not in linear form.

Bohart-Adams model and bed depth service time (BDST) model

Key considerations:

1. Dilute concentration
2. The rate of adsorption is limited by the external mass transfer

$$\ln\left(\frac{C_F}{C} - 1\right) = \ln\left[\exp\left(k_B q_m \frac{H}{u}\right) - 1\right] - k_B C_F t$$

If $\exp(k_B q_m H/u)$ is much larger than 1, it can be reduced and rearranged as

$$t = \frac{q_m}{C_F u} H - \frac{1}{k_B C_F} \ln\left(\frac{C_F}{C} - 1\right)$$

At 50% breakthrough, $C/C_F = 0.5$ and $t = t_{1/2}$, the above expression changes to

$$t_{1/2} = \frac{q_m H}{C_F u}$$

Yoon – Nelson Model

This considers that the decrease in the probability of each adsorbate to be adsorbed is proportional to the probability of its adsorption and breakthrough on the adsorbent

$$\ln \frac{C}{C_F - C} = K_{YN} t - t_{1/2} K_{YN}$$

Clark Model

Key considerations:

- The shape of the mass-transfer zone is constant
- Fluid velocity is constant (plug flow type)
- The isotherm fits the Freundlich type
- Adsorption rate is pseudo first order

$$\ln \left[\left(\frac{C_F}{C} \right)^{n-1} - 1 \right] = -r't + \ln B$$

Wolborska model

Wolborska and Pustelnik (1996) analyzed the adsorption of *p*-nitrophenol on activated carbon and found that the initial segment of the breakthrough curve is controlled by film diffusion with constant kinetic coefficient, and the concentration profile of the initial stage moves axially in the column at a constant velocity. Moreover, the width of concentration profile in the column and the final breakthrough curve were nearly constant. Based on above observations, they developed a model to describe the breakthrough at low concentration region

$$\ln \frac{C}{C_F} = \frac{\beta_L C_F \varepsilon}{\rho q_F} t - \frac{\beta_L H}{u}$$

Complete model: Hydrodynamics + Mass transport (ext.) + Adsorption

To supplement this technological implementation, knowledge of the filter dynamics (design lifetime) is important for its operation and upscaling.

1. Continuity equation $\nabla \cdot \mathbf{u} = 0$

Fluid properties
Viscosity, μ
Filter properties
Permeability, κ
Porosity, ϵ
Density, ρ

2. Hydrodynamics of porous medium (Darcy–Brinkman)

with velocity \mathbf{u} at pressure p , $[-p\mathbf{I} + \frac{\mu}{\epsilon}\nabla^2\mathbf{u} - \left(\frac{\mu}{k}\right)\mathbf{u}] = 0$

3. Convective-diffusive equation $\epsilon \left(\frac{\partial c}{\partial t} \right) + \frac{1}{\epsilon} \mathbf{u} \cdot \nabla c - D \nabla^2 c = -\rho_s \left(\frac{\partial q}{\partial t} \right)$

Contaminant transport

Contaminant removal

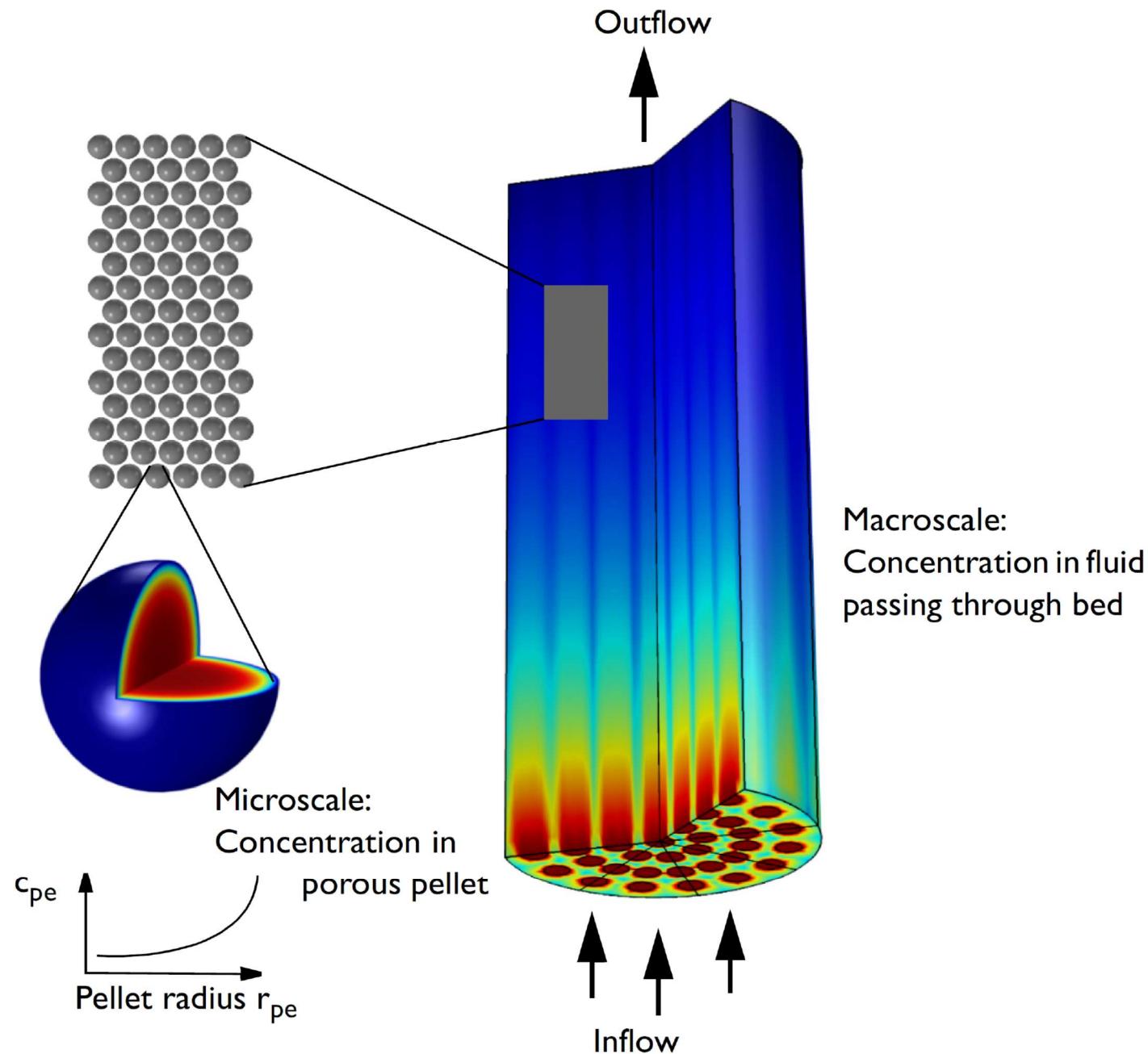
4. Adsorption dynamics, q $\frac{\partial q}{\partial t} = k^+ c (q_{max} - q) - k^- q$ Desorption
Adsorption

Model simplification: In real application, Pe is very high, $\left[\bar{u} \frac{\partial c}{\partial r} + \bar{v} \frac{\partial \bar{c}}{\partial z} \right] = -\gamma \frac{\partial \bar{q}}{\partial t}$

Advantage: single parameter γ for any system variation, $\gamma = M k^+ q_{max} / Q$

filter rating γ quantifies filter effectiveness

Multi-scale model



Complete model: Hydrodynamics + Mass transport (ext.) + Intra-particle dynamics + Adsorption

Continuity

$$\nabla \cdot \mathbf{u} = 0$$

Hydrodynamics: momentum conservation

$$-\nabla p + \frac{\mu}{\phi} \nabla^2 \mathbf{u} - \frac{\mu}{k} \mathbf{u} = 0$$

Species convective diffusive adsorption with film resistance

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = D_l \nabla^2 c - k_f \xi (c - c_p |_{r_p=a_p})$$

$$\xi = \frac{3}{a_p} (1 - \phi)$$

$$\phi_p \frac{\partial c_p}{\partial t} + (1 - \phi_p) \rho_s \frac{\partial q}{\partial t} = \frac{D_p}{r_p^2} \frac{\partial}{\partial r_p} \left(r_p^2 \frac{\partial c_p}{\partial r_p} \right)$$

Microscale dynamics: intrapellet diffusion and adsorption

$$k_f (c - c_p |_{r_p=a_p}) = \phi_p D_p \frac{\partial c_p}{\partial r_p}$$

Mass transfer: film diffusion

$$Sh = 2 + 0.5 Re_p^{1/2} Sc_p^{1/3}$$

Adsorption kinetics

$$\frac{\partial q}{\partial t} = k_1 c_p (q_{max} - q) - k_2 q$$

Complete model: Hydrodynamics + Mass transport (ext.) + Intra-particle dynamics + Adsorption

$Sh = \frac{1.1}{\varepsilon} Pe^{1/3}$	–	(Tan <i>et al.</i> , 1975)
$Sh = \frac{1.09}{\varepsilon} Pe^{1/3}$	$0.0016 < \varepsilon Re < 55;$ $950 < Sc < 70000$	(Wilson and Geankoplis, 1966)
$Sh = 2 + 1.58 Re^{0.4} Sc^{1/3}$	$0.001 < Re < 5.8$ $5.8 < Re < 500$	(Ohashi <i>et al.</i> , 1981)
$Sh = 2 + 1.21 Re^{0.5} Sc^{1/3}$	$Re > 500$	
$Sh = 2 + 0.59 Re^{0.6} Sc^{1/3}$	$0.08 < Re < 125;$ $150 < Sc < 1300$	(Williamson <i>et al.</i> , 1963)
$Sh = 2.4 \varepsilon Re^{0.3} Sc^{0.42}$	–	(Ko <i>et al.</i> , 2003)
$Sh = \frac{0.325}{\varepsilon Re^{0.36} Sc^{1/3}}$		
$Sh = 2 + 1.1 Re^{0.6} Sc^{1/3}$	$3.0 < Re < 10000$	(Wakao and Funazkri, 1978)
$Sh = 1.85[(1 - \varepsilon) / \varepsilon]^{1/3} Re^{1/3} Sc^{1/3}$	$Re[\varepsilon/(1 - \varepsilon)] < 100$	(Kataoka <i>et al.</i> , 1972)
$Sh = (2 + 0.644 Re^{1/2} Sc^{1/3})[1 + 1.5(1 - \varepsilon)]$	–	(Chern and Chien, 2002)
$Sh = \left[2 + \left(Sh_L^2 + Sh_T^2 \right)^{0.5} \right] [1 + 1.5(1 - \varepsilon)],$ $Sh_L = 0.644 Re^{1/2} Sc^{1/3},$ $Sh_T = (0.037 Re^{0.8} Sc) / \left[1 + 2.443 Re^{-0.1} (Sc^{2/3} - 1) \right]$	$Re Sc > 500;$ $Sc < 12000$	(Gnielinski, 1978)

Choice of models

Regression analysis for the best fit, $R^2 = \frac{\sum \left[\left(\frac{C}{C_F} \right)_{mod} - \left(\frac{C}{C_F} \right)_{expt} \right]^2}{N}$

