Batch system example (*previous midterm question*)

You are to design a batch adsorber to remove an organic contaminant (A) from 400L of aqueous solution containing 0.05g/L of the contaminant. To facilitate this you do a bench scale experiment with 1L solution at the same concentration (0.05g/L) and 3g of an adsorbent. In the bench scale experiment you find that 96% of the contaminant was removed. You need to remove 99% of the contaminant in the full scale apparatus. You can assume that a linear isotherm applies.

For the full scale system:

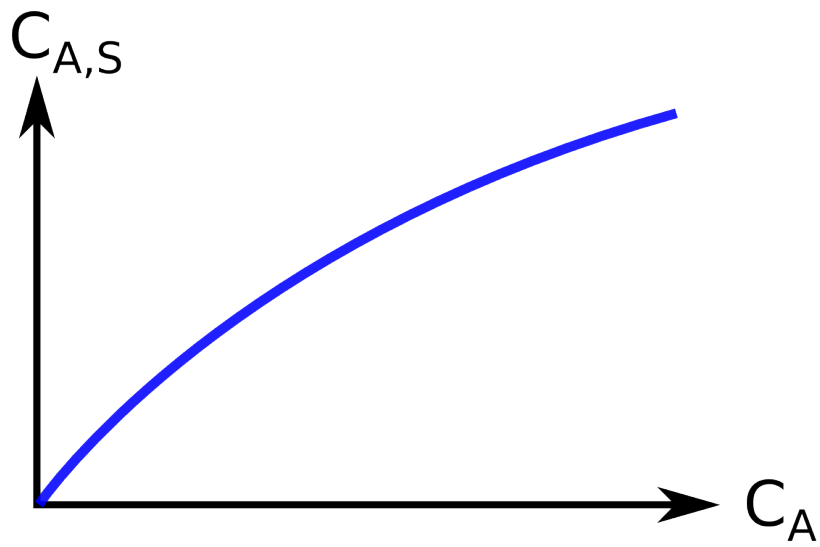
1. At the end of the batch, what will be the concentration of the solution in the adsorber and concentration of A on the adsorbent?
2. How much adsorbent do you need? [Ans: 4.95 kg]

Equilibrium modelling: Freundlich model

Freundlich isotherm

$$C_{A,S} = K\,(C_A)^{1/m} \qquad \text{for } 1 < m < 5$$

- It is an empirical model, but it works well



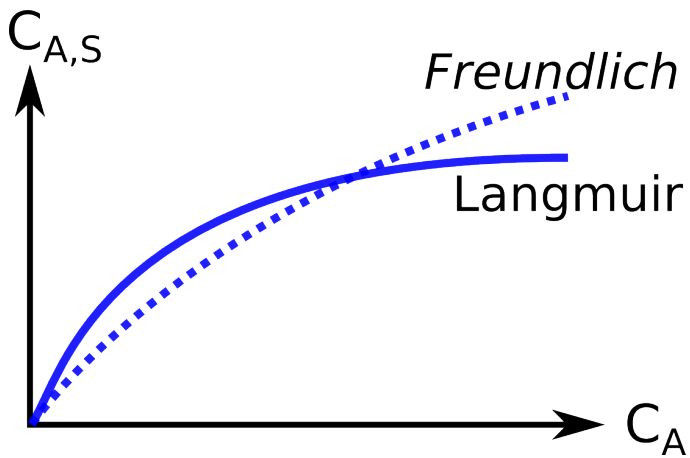
- Constants determined from a log-log plot
- How would you go about setting up a lab experiment to collect data to calculate K?
- Which way will the isotherm shift if temperature is increased?

Equilibrium modelling: Langmuir isotherm

- we have a uniform adsorbent surface available (all sites equally attractive)
- there are a total number of sites available for adsorbate A to adsorb to
- C_T = total sites available $\left[\frac{\text{mol sites}}{\text{kg adsorbate}}\right]$
- C_V = vacant sites available $\left[\frac{\text{mol sites}}{\text{kg adsorbate}}\right]$
- rate of adsorption $= k_A P_A C_V$ = proportional to number of collisions of A with site S
- $C_{A,S}$ = sites occupied by A $\left[\frac{\text{mol sites}}{\text{kg adsorbate}}\right]$
- assuming 1 site per molecule of A, and only a monolayer forms
- rate of desorption$= k_{-A} C_{A,S}$ = proportional to number of occupied sites
- net rate $= k_A P_A C_V - k_{-A} C_{A,S}$

Equilibrium modelling: Langmuir isotherm

- Net rate $= k_A P_A C_V - k_{-A} C_{A,S}$
- define $K_A = \dfrac{k_A}{k_{-A}}$
- essentially an equilibrium constant: $A + S \rightleftharpoons A \cdot S$
- at equilibrium, the net rate is zero
- implying $\dfrac{k_A C_{A,S}}{K_A} = k_A P_A C_V$
- but total sites $= C_T = C_V + C_{A,S}$
- so $\dfrac{k_A C_{A,S}}{K_A} = k_A P_A (C_T - C_{A,S})$
- simplifying: $C_{A,S} = K_A P_A (C_T - C_{A,S})$
- then $\boxed{C_{A,S} = \dfrac{K_A C_T P_A}{1 + K_A P_A} = \dfrac{K_1 P_A}{1 + K_2 P_A} = \dfrac{K_3 C_A}{1 + K_4 C_A}}$
- Fit data using Eadie-Hofstee diagram or nonlinear regression
- Same structure as Michaelis-Menten model (bio people)



Summary of isotherms

We aren't always sure which isotherm fits a given adsorbate-adsorbent pair:

1. Perform a laboratory experiment to collect the data
2. Postulate a model (e.g. linear, or Langmuir)
3. Fit the model to the data
4. Good fit?

Other isotherms have been proposed:

- BET (Brunauer, Emmett and Teller) isotherm
- Gibb's isotherm: allows for a multilayer of adsorbate forming

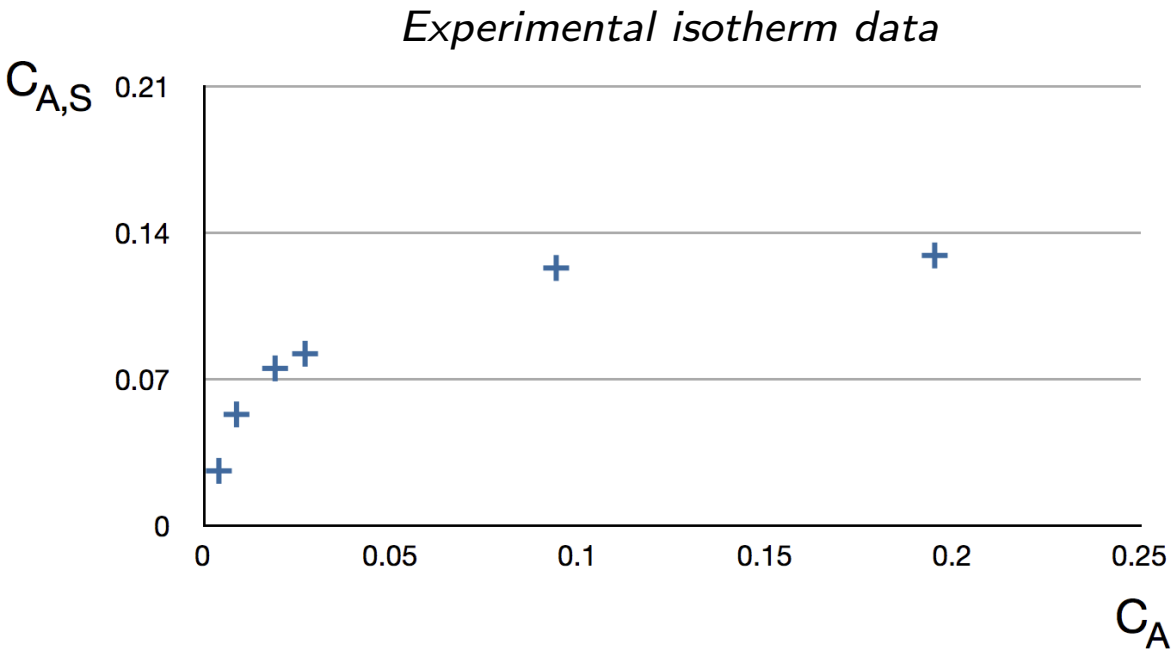
These are far more flexible models (more parameters); e.g. Langmuir isotherm is a special case of the BET isotherm.

Further questions to try

Adapted from Geankoplis question 12.2-1

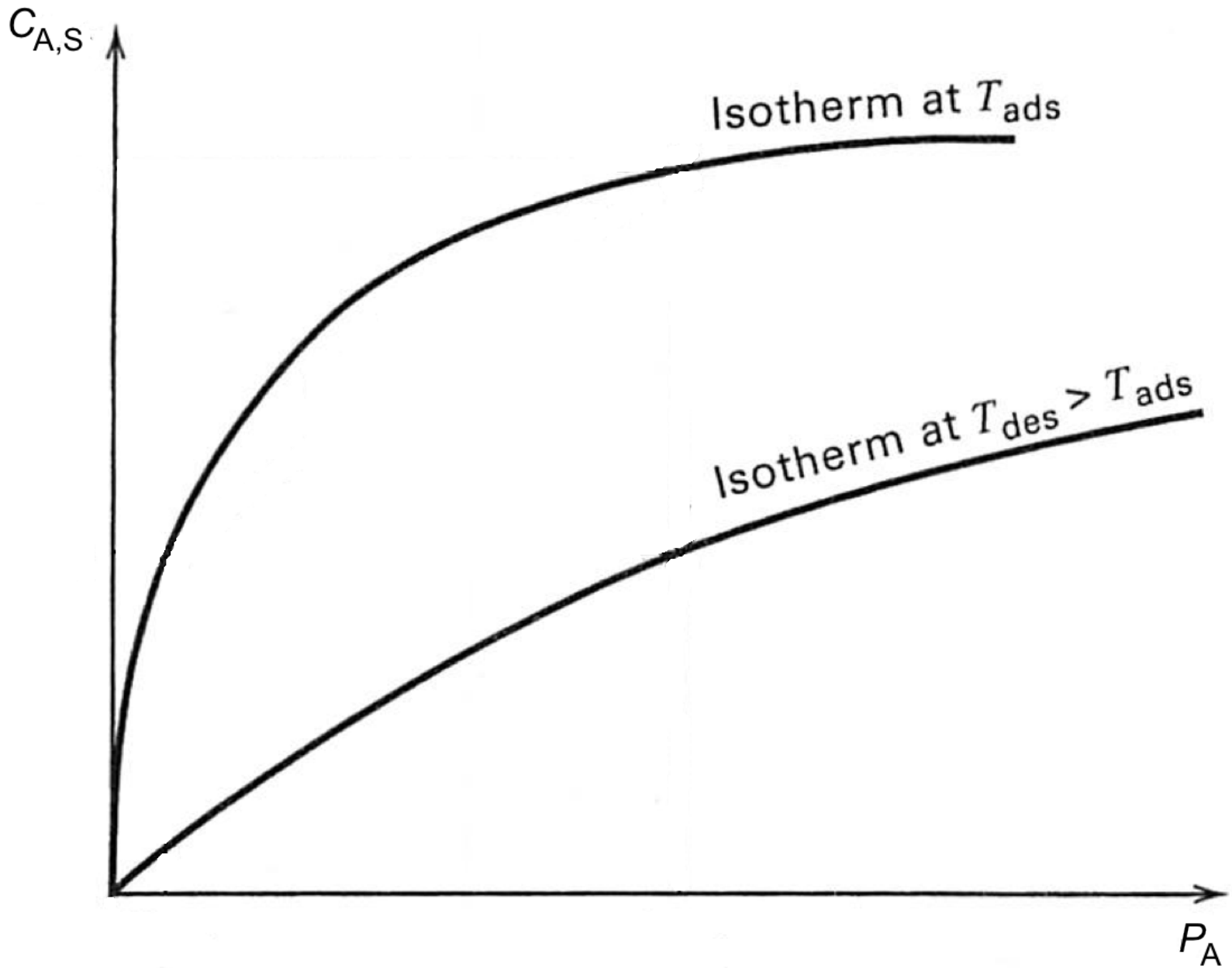
2.5 m^3 of wastewater solution with 0.25 kg phenol/m^3 is mixed with 3.0 kg granular activated carbon until equilibrium is reached. Use the following isotherm, determined from lab values, to calculate the final equilibrium values of phenol extracted and percent recovery. Show the operating point on the isotherm. Units of C_A are [kg per m^3] and $C_{A,S}$ is in [kg solute per kg of activated carbon].

[Ans: $C_A \approx 0.10$ kg per m^3, $C_{A,S} \approx 0.12$ kg/kg, recovery = 58%]



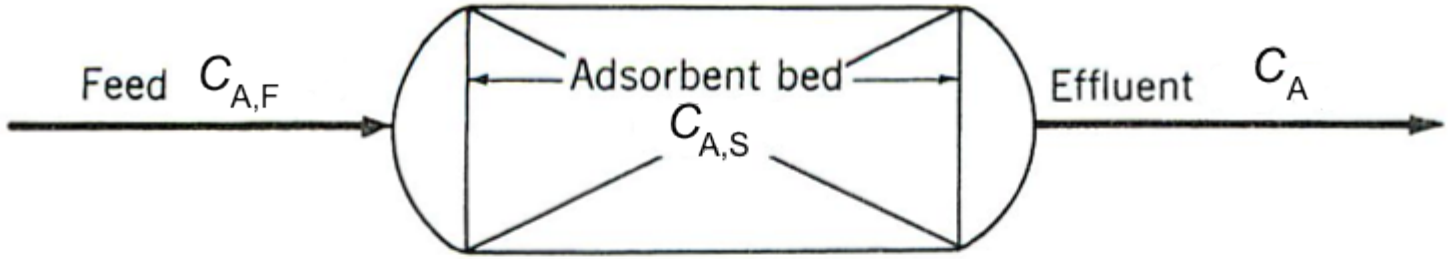
$$C_{A,S} = \frac{0.145 C_A}{0.0174 + C_A}$$

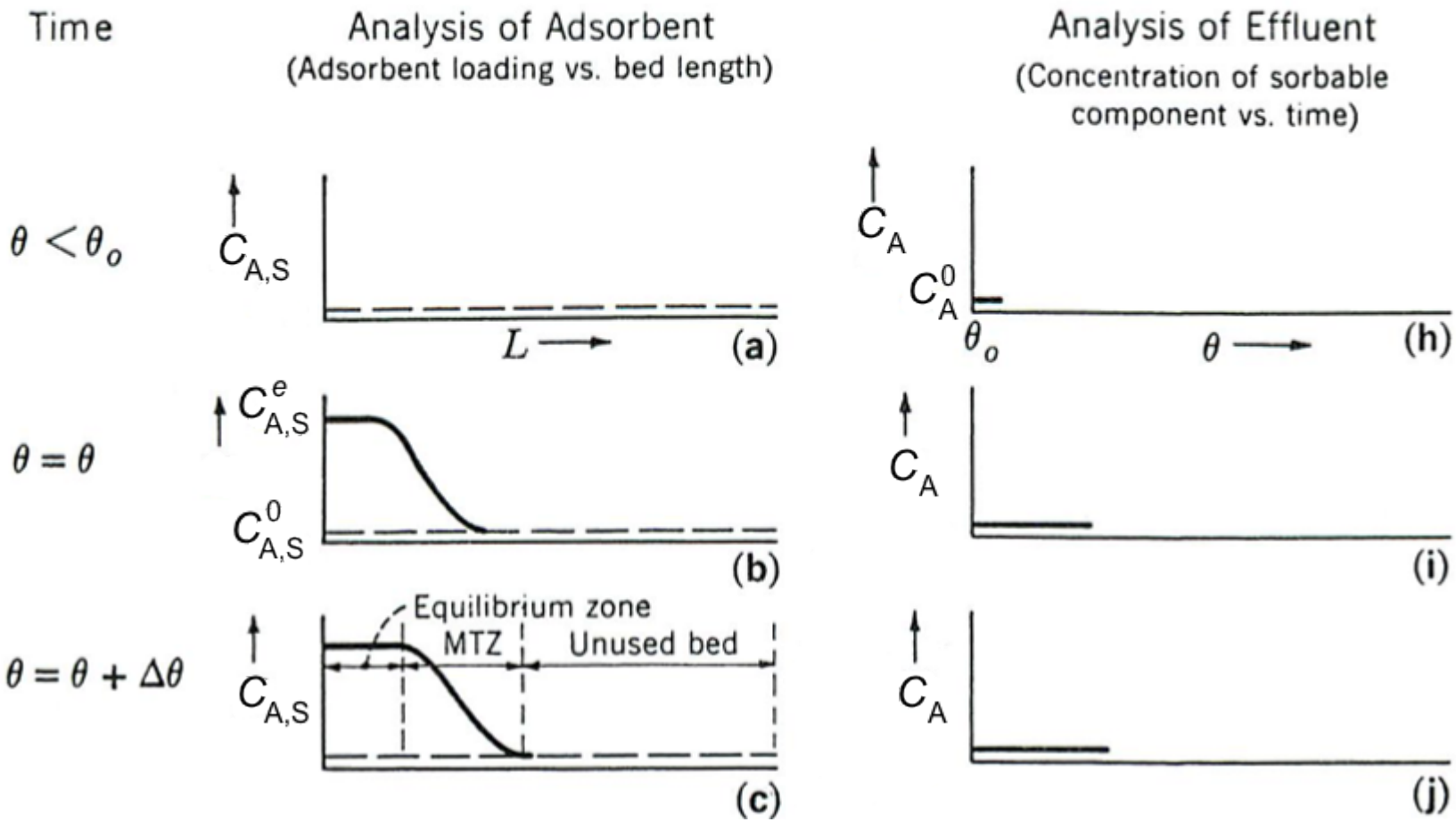
Isotherms change at different temperatures



[Seader, 3ed, p610]

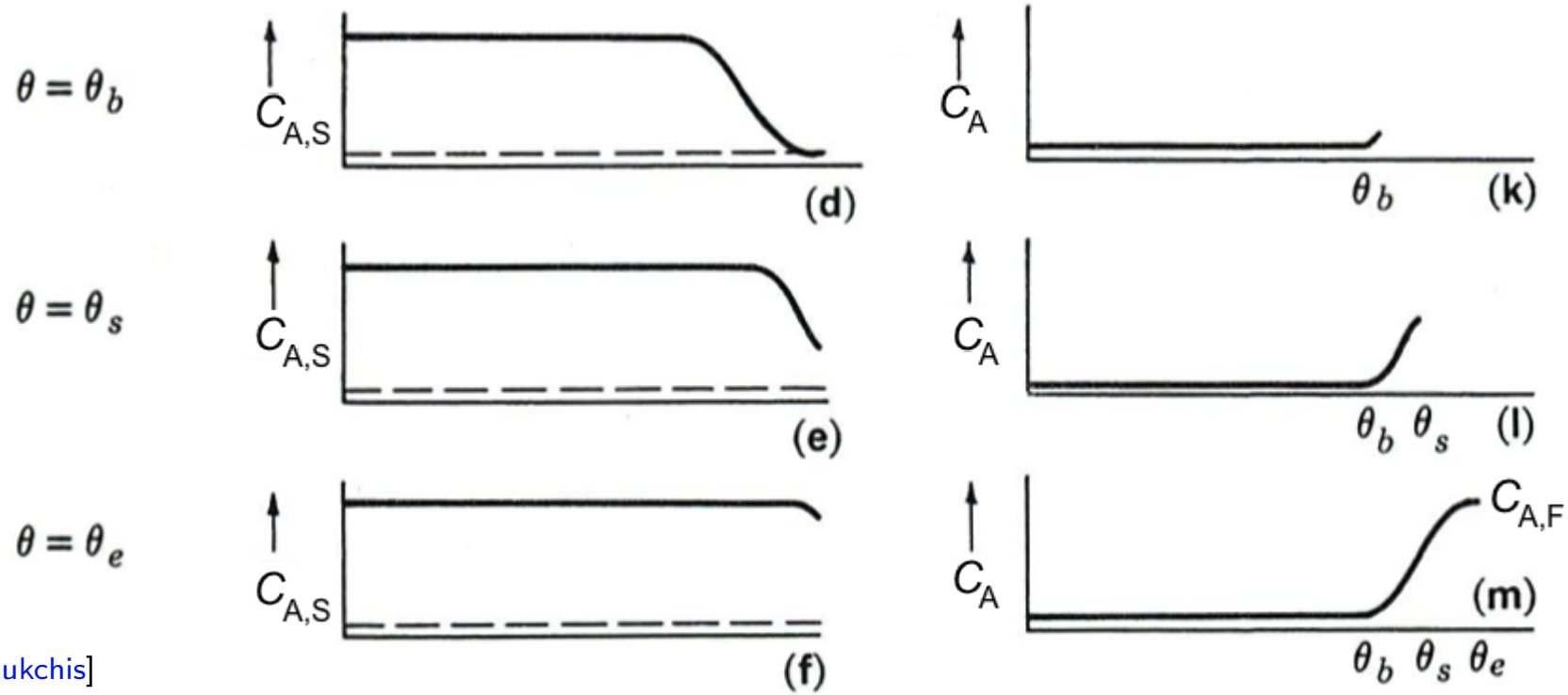
Understanding adsorption in packed beds (1 of 2)





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

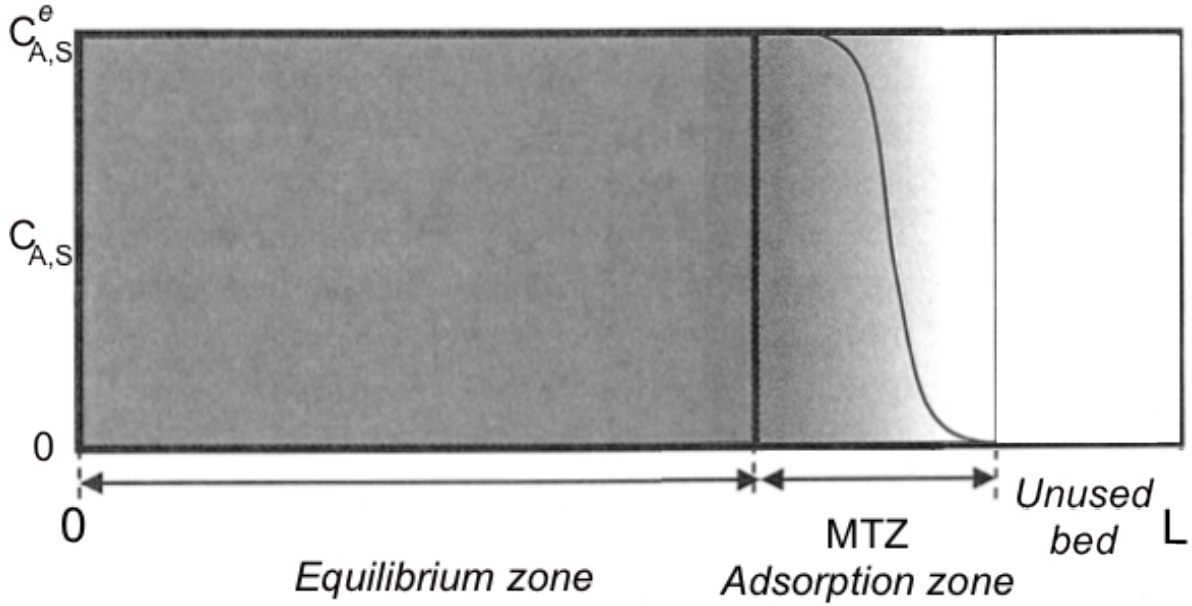
Understanding adsorption in packed beds (2 of 2)



[Lukchis]

- $C_{A,S}$ = concentration of adsorbate on adsorbent
- $C^e_{A,S}$ = concentration at equilibrium on the adsorbent (equil loading)
- $C^0_{A,S}$ = concentration on the regenerated adsorbent at time 0
- θ_b = breakthrough time: "*time to stop using the packed bed!*"; usually when $C_A = 0.05 C_{A,F}$
- 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

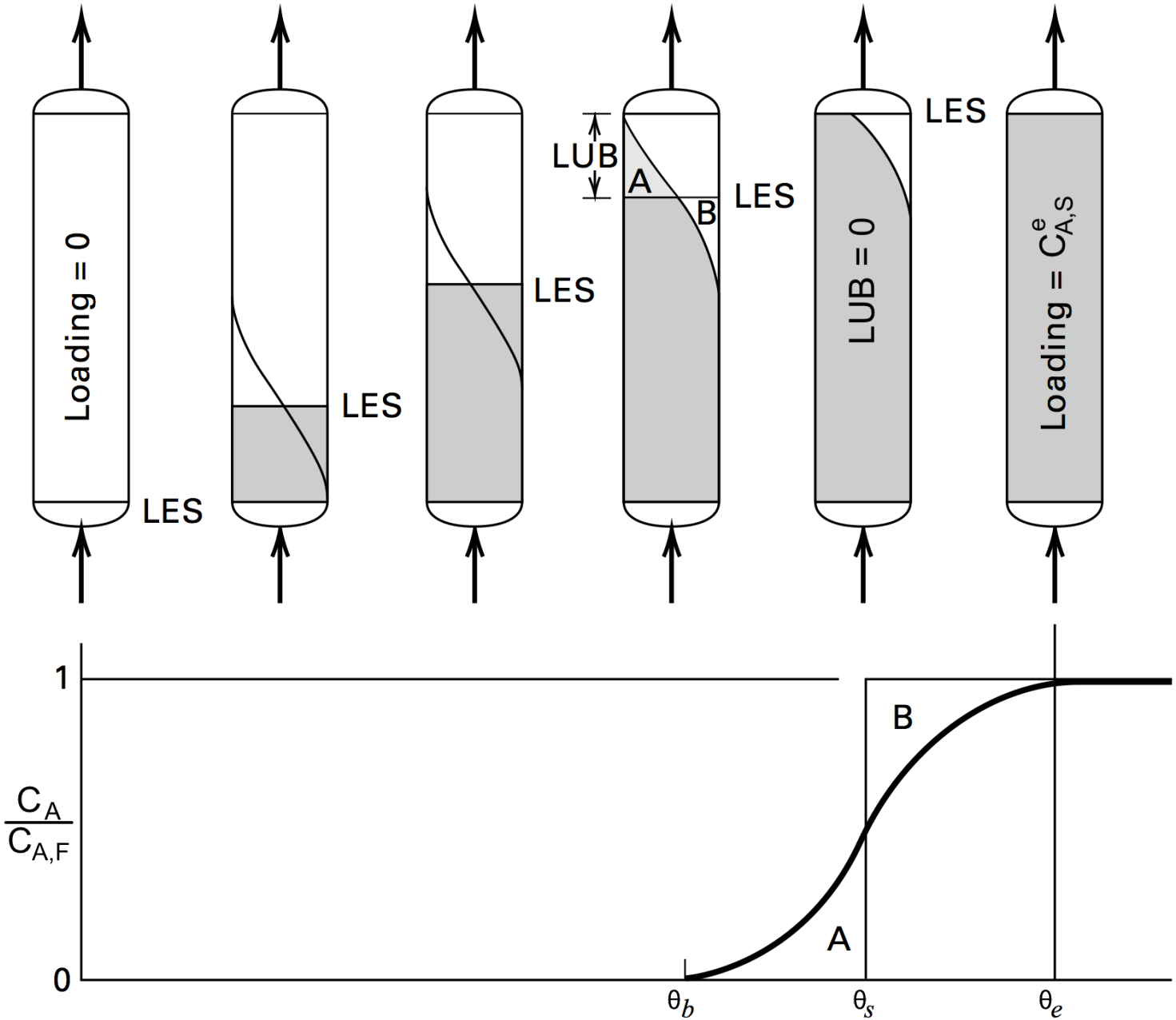
Bed concentration just prior to breakthrough



[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 $C_{A,F}$.

Figures to help with the next example



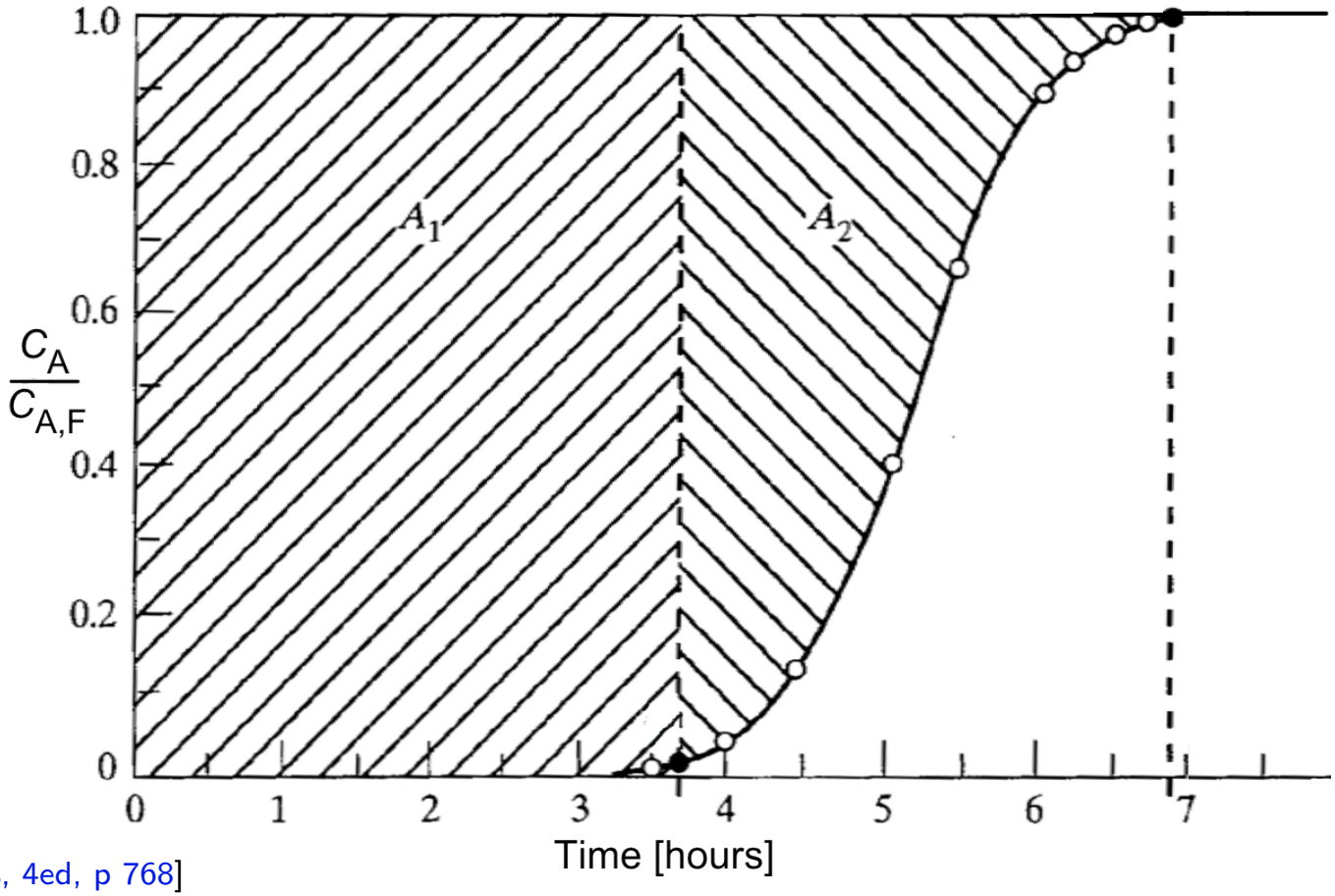
[Seader, Henly, Roper, p 605]

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)

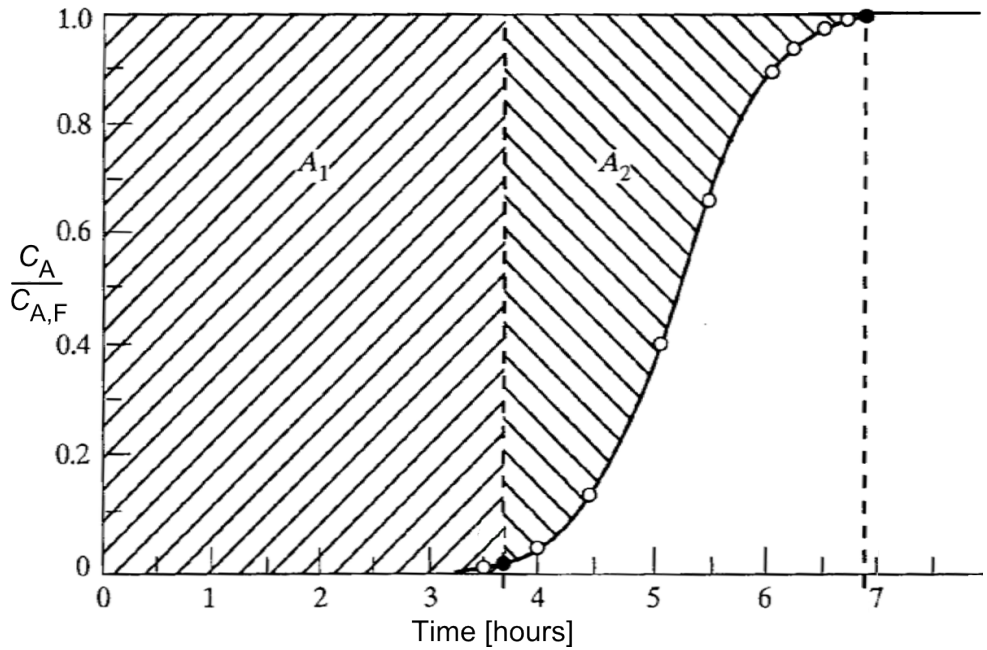
An adsorbate in vapour is adsorbed in an experimental packed bed. The inlet contains $C_{A,F} = 600$ ppm of adsorbate. Data measuring the outlet concentration over time from the bed are plotted below:



[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 wavefront (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

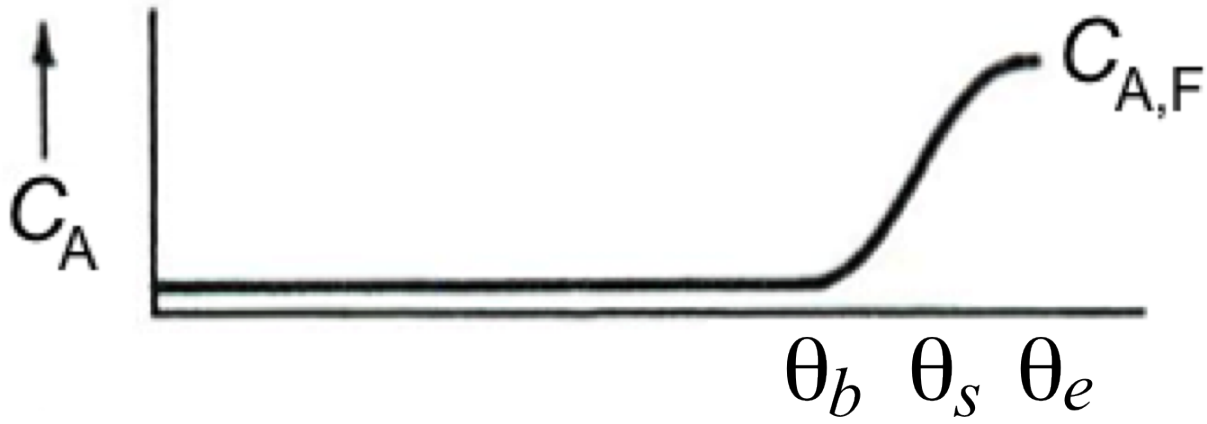


3. How long does it take to reach this ideal capacity? ≈3.65 hours

Ignore the tiny part missing from the integrated area.

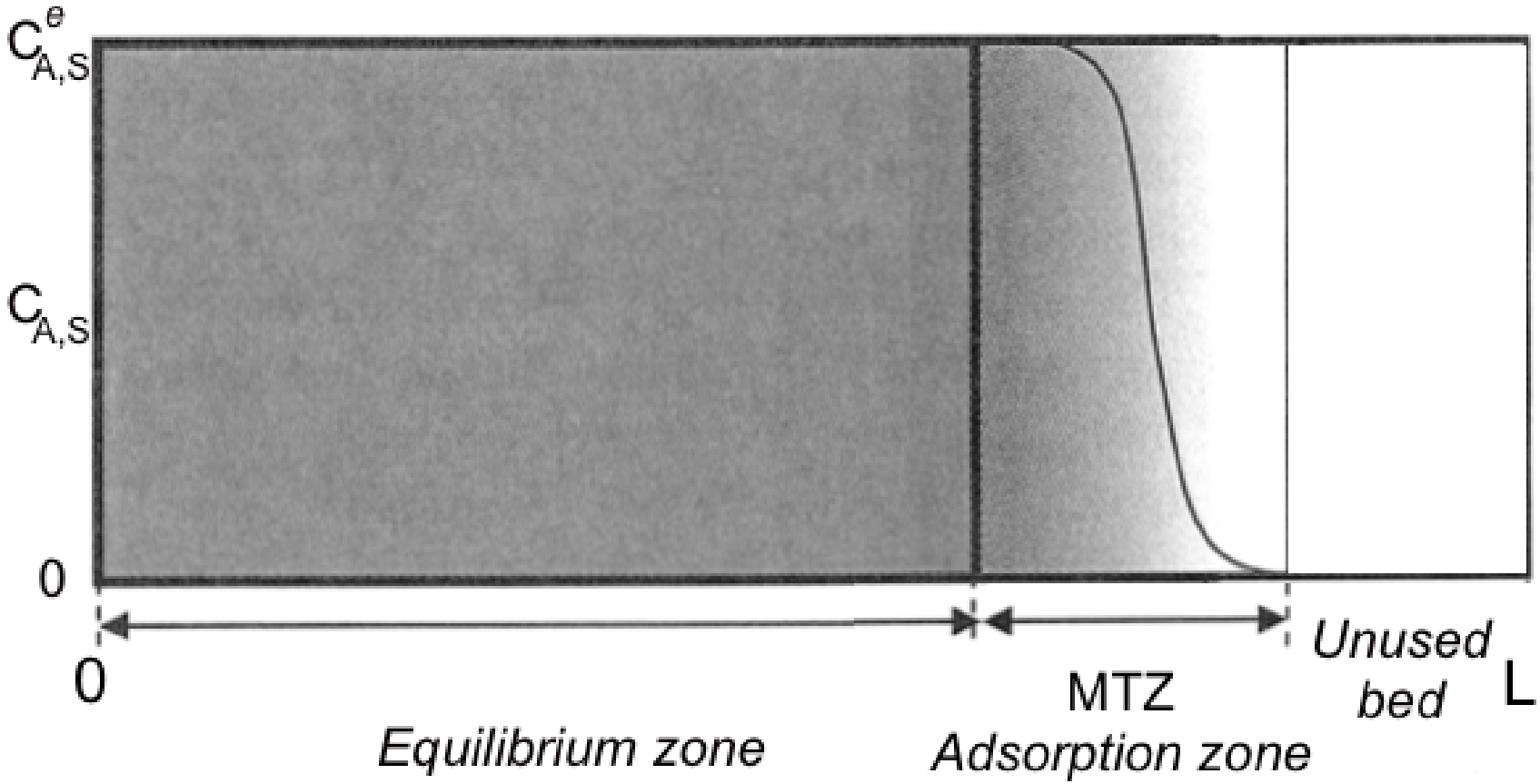
Example

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
- $\theta_S = \int_0^\infty \left(1 - \frac{C_A}{C_{A,F}}\right) dt =$ shaded area $= A_1 + A_2 = 3.65 + 1.55 = 5.20$ 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: $14(1 - 0.75) = 3.5$ cm
   - LUB = length of unused bed = 3.5 cm
   - LES = length of equilibrium section = the used up part = $14.0 - 3.5 = 10.5$ 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	$0.75 \times 14 = 10.5$cm	21.6cm
LUB	$0.25 \times 14 = 3.5$cm	3.5cm
Total	14cm	25.1cm

- Ratio LES lengths to breakthrough times: $\dfrac{\text{LES}^{\text{des}}}{\text{LES}^{\text{curr}}} = \dfrac{\theta_b^{\text{des}}}{\theta_b^{\text{curr}}}$
- Length to get to breakthrough in 7.5 hours $= \text{LES}^{\text{des}} = 21.6$ cm
- We have to add on the length of the unused bed $= 4.1$ cm from before (same diameter, same flow profile!)
- So new bed length $=$ LES $+$ LUB $= 21.6 + 4.1 =$ 25.1 cm
- LUB is the same length, provided all other conditions are the same
- Then fraction actually used $= \dfrac{21.6}{24.5} = 0.88$ (compared to 0.75)

Bed mass balance

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

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

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

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

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

Modified from a previous exam

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? [Ans: 22.66kg]
2. How long it will take to reach this detectable outlet concentration? [15.7 days]

Regenerating the bed

Aim

To remove adsorbate from the packed bed.

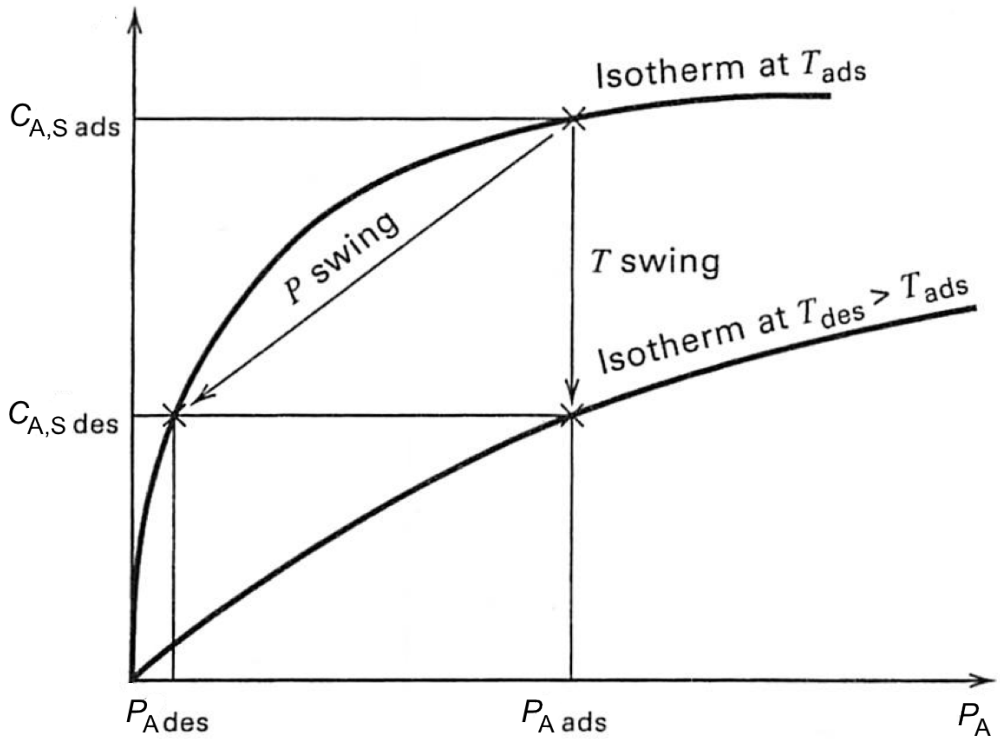
1: Temperature swing adsorption (TSA)

- heat the bed: usually steam is used (due to high latent heat)
  - why add heat? (recall, heat is released during adsorption)
- creates a thermal wave through the packed bed
- isotherm at higher temperature is shifted down
- causes the adsorbate to be diluted in the stripping fluid
- often leave some residual adsorbate behind, since time to completely strip adsorbent of it would be excessive
- care must be taken with flammable adsorbates:
  - stripping temperatures are high
  - often near flammable limits
  - carbon beds have been known to catch fire

See illustration on next page

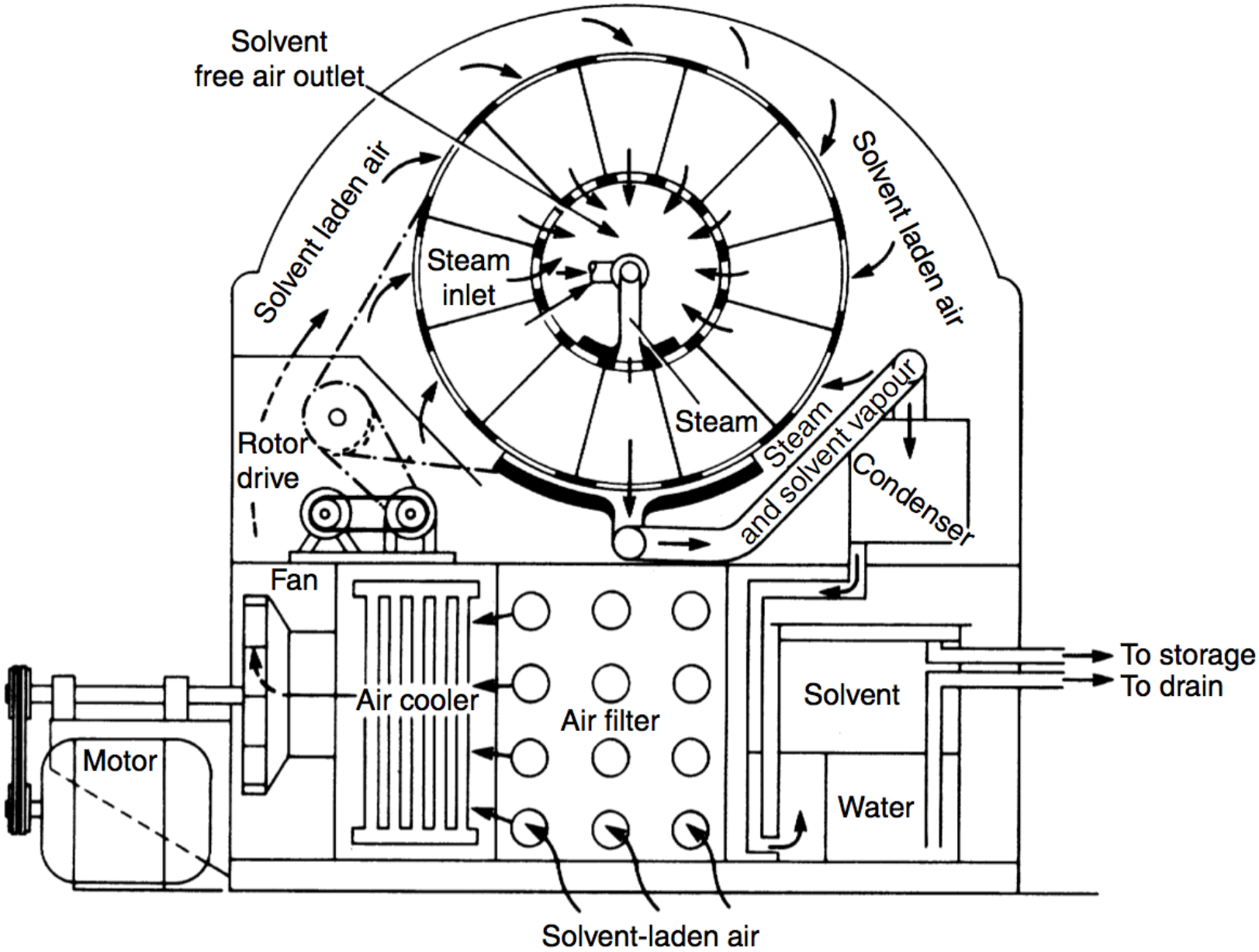
Regenerating the bed

2. Pressure swing adsorption (PSA)
   - used when the "product" is the cleaned (stripped) fluid
   - add feed with adsorbate at high pressure (loads the adsorbate)
   - drop the pressure and the adsorbate starts to desorb
   - run two beds in parallel (one desorbing, the other adsorbing)
   - widely used for portable oxygen generation, H_2S capture in refineries



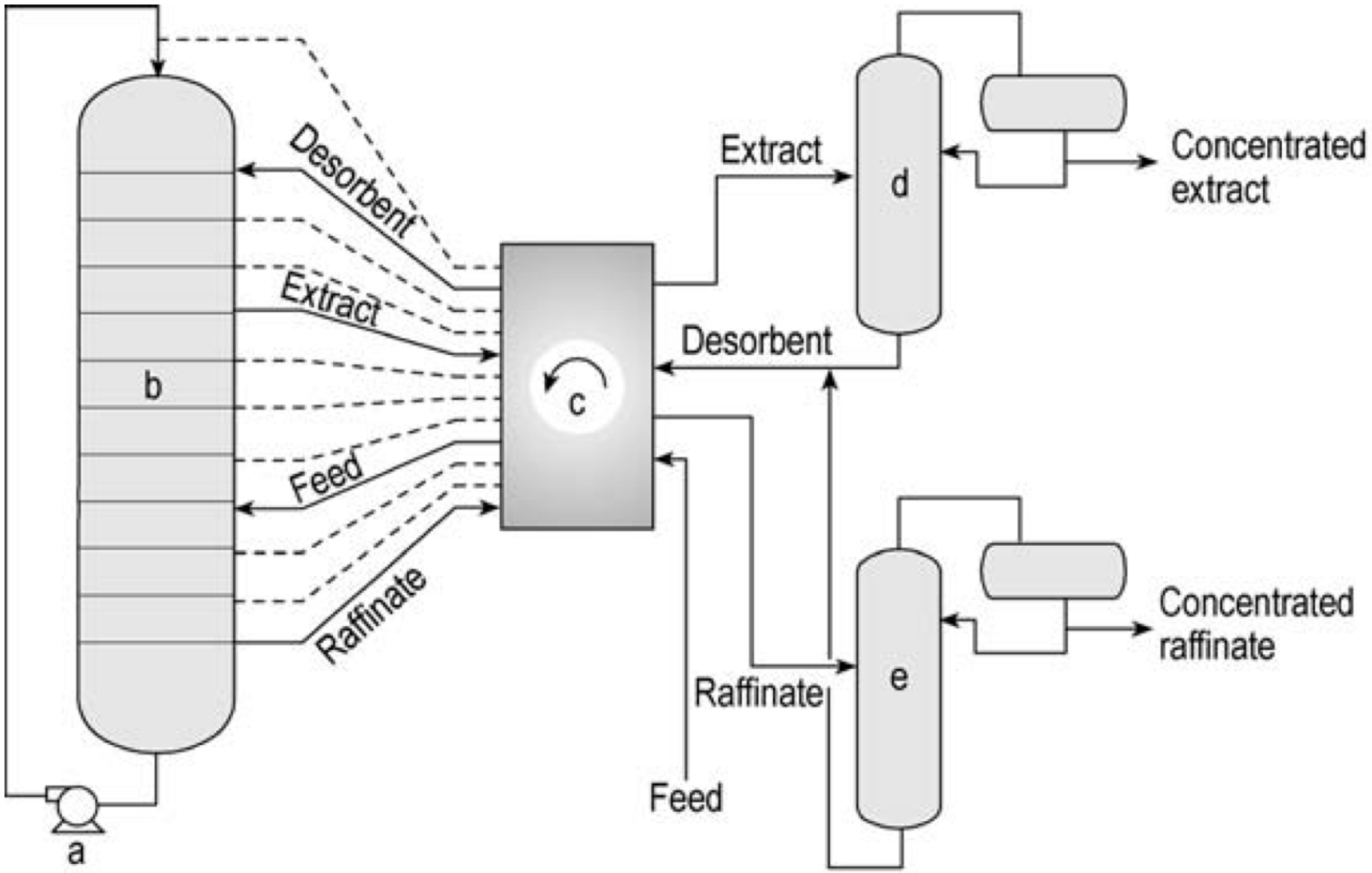
[Seader, 3ed, p610]

Rotary devices



[Richardson and Harker, p 1034]

Adsorption equipment: Sorbex column



[Uhlmanns, p 560]

a) Pump; b) Adsorbent chamber; c) Rotary valve; d) Extract column; e) Raffinate column