# CE407 SEPARATIONS

Lecture 25

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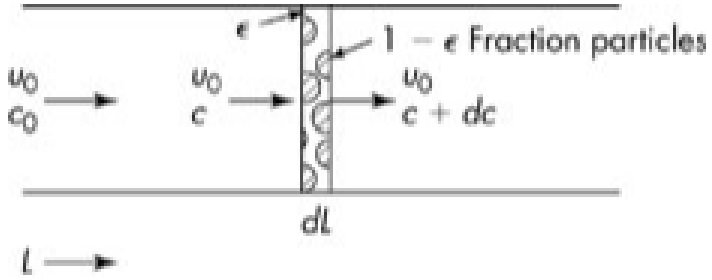
# Adsorption Fundamentals

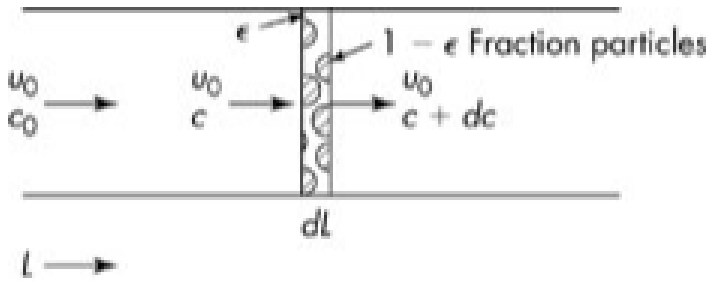
- The last lecture looked at Adsorption as an observation of typical results
- Today we will look at it from more of a viewpoint of fundamental principles
  - *Did someone say "Material Balances"?*




- The concentration of solute in the solution, $c$, is changing because the solute is being adsorbed onto the surface of the adsorbent solid
- The change in superficial velocity is small for a dilute solution and we will treat it as a constant, $u_0$
- $\epsilon$ is the external void fraction (i.e. How much open space exists around the particles)
- $(1 - \epsilon)$ is the fraction of space taken up by the adsorbent particles

# Adsorption Fundamentals

- The change in the amount of solute per unit cross-sectional area is:




$$u_0\, c \;-\; u_0\,(c + dc) = -u_0\, dc$$

what goes in the control volume – what leaves the control volume = change in amount in control volume

- The change in the amount of solute results from two different causes:

1) **The change in the fluid concentration**

$$\epsilon\, dl\, \frac{\partial c}{\partial t}$$

$\epsilon\, dl$ is the volume of fluid in the control volume per unit cross-sectional area

$\frac{\partial c}{\partial t}$ is the change in concentration (mass/volume) with respect to time

2) **The change in surface adsorption**

$$(1 - \epsilon)\, dl\, \rho_p\, \frac{\partial w}{\partial t}$$

# Adsorption Fundamentals

- The change in surface adsorption

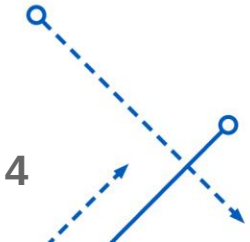
$$(1 - \epsilon)\, dl\, \rho_p \frac{\partial w}{\partial t}$$

  - $(1 - \epsilon)\, dl$ is the volume occupied by particles in the control volume per unit cross-sectional area
  - $\rho_p$ is the mass of particles per unit volume
  - $(1 - \epsilon)\, dl\, \rho_p$ is the mass of particles in the control volume per unit cross-sectional area
  - $\frac{\partial w}{\partial t}$ is the change with respect to time of the $\frac{mass\ of\ solute\ adsorbed}{mass\ of\ adsorbent\ particles}$

- The two causes added to one another must equal the change in the amount of solute in the control volume per unit cross-sectional area, therefore we arrive at this partial differential equation:

$$\epsilon\, \partial l \frac{\partial c}{\partial t} + (1 - \epsilon)\, \partial l\, \rho_p \frac{\partial w}{\partial t} = -u_0\, dc$$

$$\boxed{\epsilon \frac{\partial c}{\partial t} + (1 - \epsilon)\, \rho_p \frac{\partial w}{\partial t} = -u_0 \frac{\partial c}{\partial l}}$$



# Mass Transfer to Adsorbent Particles

Three Steps:

1) Diffusion through film layer around the particle
2) Diffusion through pores into internal surfaces
3) Actual adsorption step
   - Practically instantaneous relative to steps 1) and 2)

Particle with film layer  Close up of layer

This can be modeled as:

$$(1 - \epsilon)\,\rho_p \frac{\partial w}{\partial t} = K_c\, a\, (c - c^*)$$

$a$ is the external surface area of the particles

$c^*$ is the concentration value in equilibrium with $w$

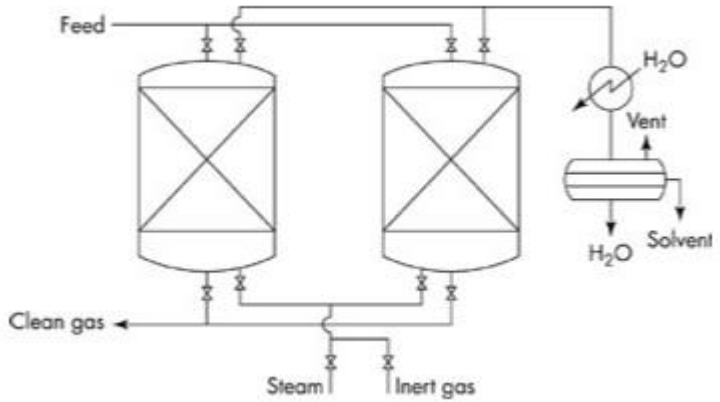
- Obtained via the isotherm

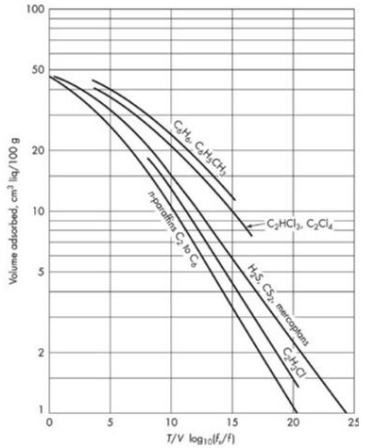
$$\frac{1}{K_c} = \frac{1}{k_{c_{ext}}} + \frac{1}{k_{c_{int}}} = \frac{1}{Film\ Resistance} + \frac{1}{Pore\ Resistance}$$

- These equations are not generally solvable, but there are special cases that can be worked out

# Regeneration

- If the particles and the product can withstand high temperatures, then you can use heat to release the product from the adsorbent




- At higher temperature the equilibrium shifts and the adsorbent releases the solute
- Use a back flow of steam or air (if the materials are all non-flammable) or $N_2$
- Regeneration is stopped soon after the temperature front reaches the feed entrance
  - A significant amount of adsorbed material remains which means breakthrough time is reduced
  - Exit end is almost fully regenerated so that high percentage removal of solute is still possible
  - Balance of energy cost per cycle versus length of cycle

This problem deals with some experiments performed in Elroy Hutch's laboratory on adsorption of n-hexanol from air in a 10 cm long carbon-filled bed. Measured concentration profiles are shown in Fig. 1 for various times after the initial time t = 0, with x = distance along bed.

Details of the experiment are as follows:

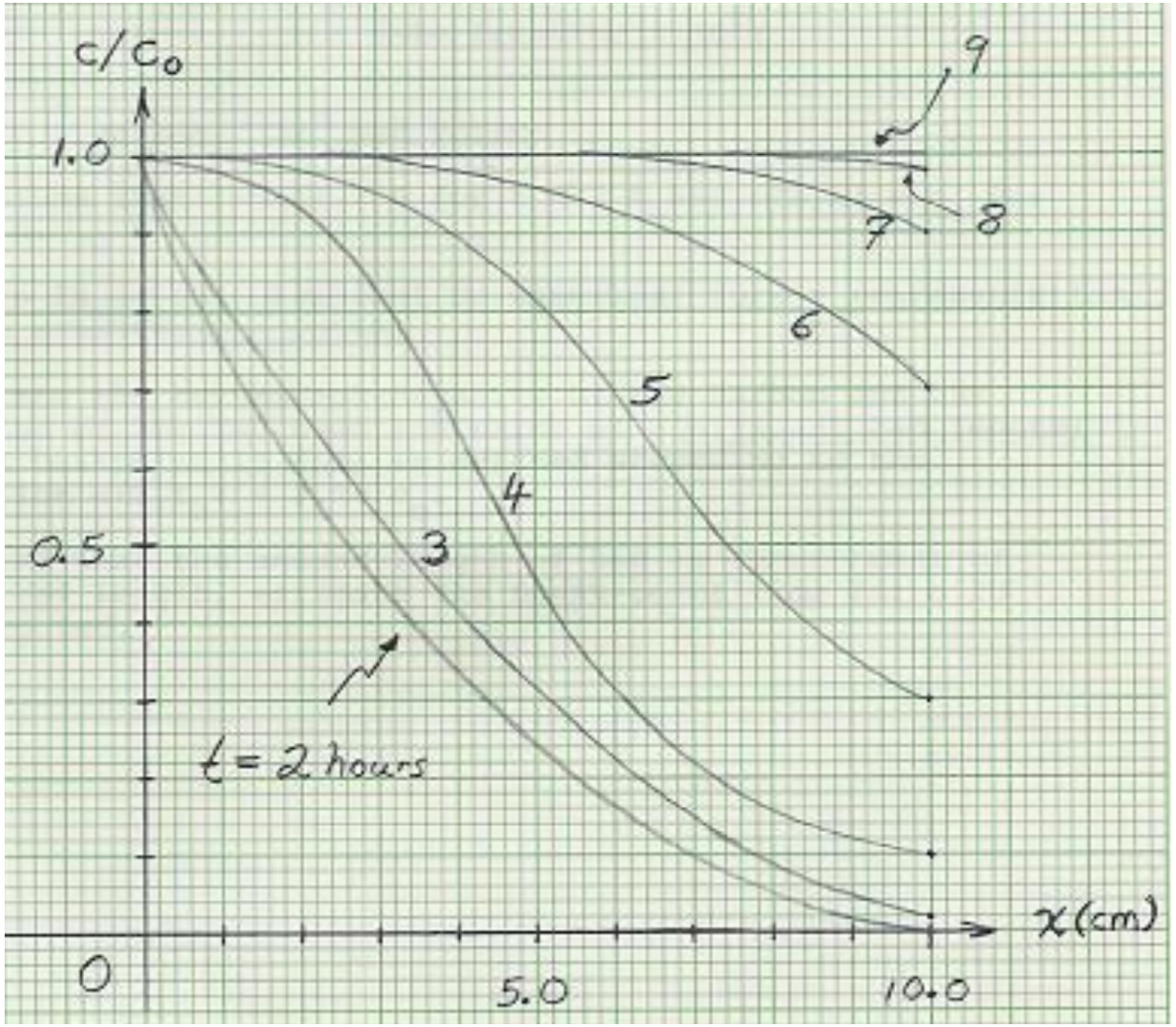
$u_o$ = superficial gas velocity = 72 cm / s
$c_o$ = 250 ppm hexanol (ppm = mole fraction x $10^6$)
$T_o$ = 50 °C
P = 690 mm Hg
$\rho_{bed}$ = 0.45 g carbon / $cm^3$ bed volume

You may assume that $c(L,t) = 0$ for $t \leq 2$ h and $c(L,t) = c_o$ for for $t \geq 9$ h.

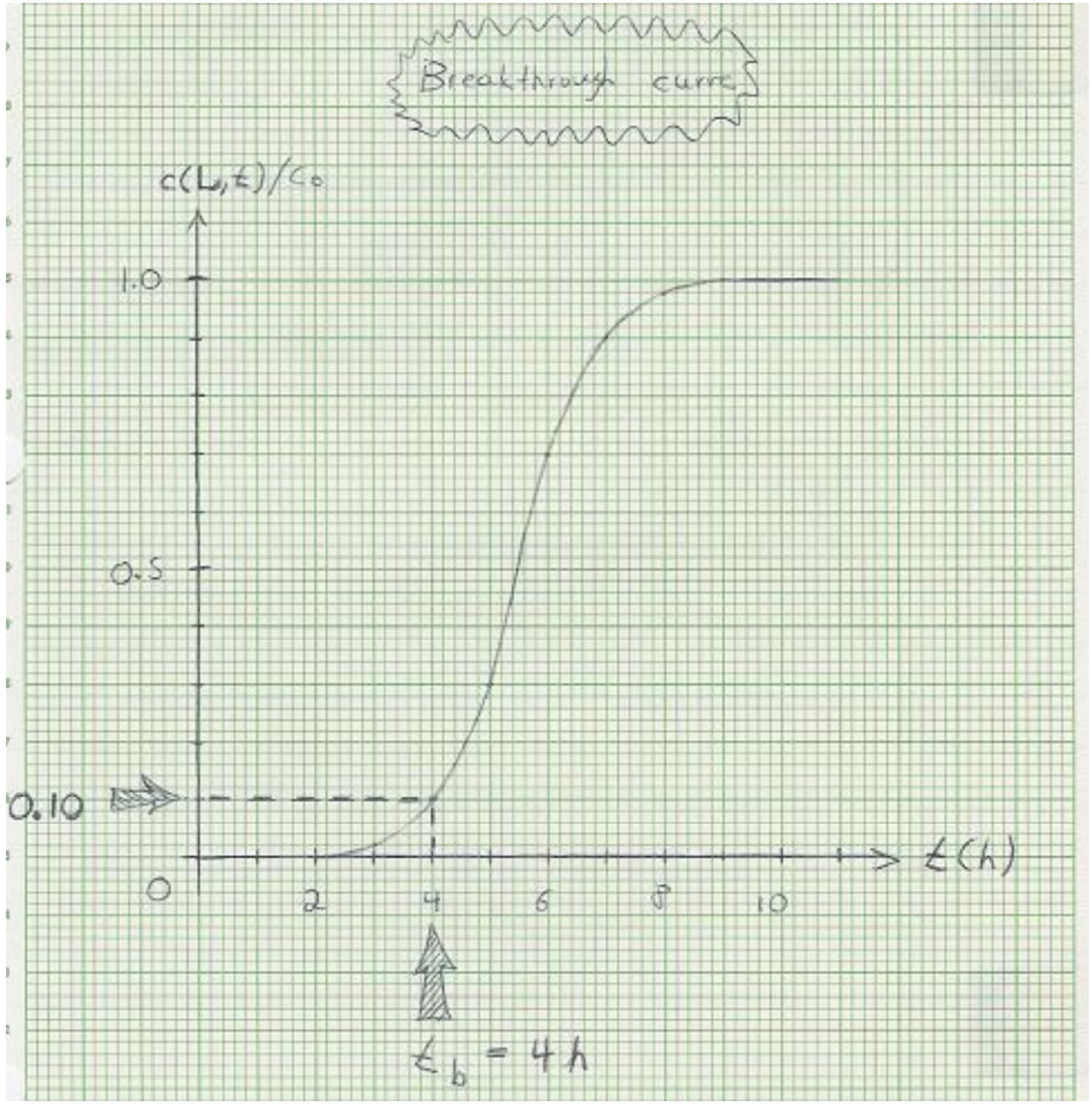
(a) Prepare in either graphical or numerical form a representation of the breakthrough curve.

(b) Calculate the saturation capacity of the carbon and the fraction of the bed used (in terms of equivalent bed length) at the beakpoint if this is defined according to the criterion $c(L,t_b) = 0.10\ c_o$.

(c) Assuming that the unused length of bed is independent of total bed length, estimate the break-point time for a 20 cm long bed.




| t (h) | c(L,t)/C₀ |
|---|---|
| 0 | 0 |
| 2 | 0 |
| 3 | 0.02 |
| 4 | 0.10 |
| 5 | 0.30 |
| 6 | 0.70 |
| 7 | 0.90 |
| 8 | 0.98 |
| 9 | 1 |
| (all later times | 1 ) |


Breakthrough curve
c(L,t)/c0
1.0
0.5
0.10
0
2
4
6
8
10
t(h)
tb = 4 h

$$w(t) = \frac{\int_0^t F_{A\,in}\left(1 - \frac{c}{c_0}\right) dt}{L\,\rho_{bed}}$$

$$\frac{w_b}{w_{sat}} = fraction\ of\ bed\ utilized$$

| $t$ (h) | $C(L,t)/C_0$ | $1-\frac{C}{C_0}$ | contribution to integral $\int_0^t (1-\frac{C}{C_0})dt$ (h) | |
|---|---|---|---|---|
| 0 | 0 | 1 | 2 | upto breakpoint |
| 2 | 0 | 1 | 0.99 | |
| 3 | 0.02 | 0.98 | 0.94 | |
| 4 | 0.10 | 0.90 | 0.80 | |
| 5 | 0.30 | 0.70 | 0.50 | |
| 6 | 0.70 | 0.30 | 0.20 | |
| 7 | 0.90 | 0.10 | 0.06 | |
| 8 | 0.98 | 0.02 | 0.01 | |
| 9 | 1 | 0 | | |

(c)

$$t_{b\,2}/t_{b\,1} = \frac{L_2 * \left(1 - \frac{LUB}{L_2}\right)}{L_1 * \left(1 - \frac{LUB}{L_1}\right)}$$

This problem deals with some experiments performed in Elroy Hutch's laboratory on adsorption of water from air in a bed filled with silica gel (length L = 60 cm). Measured concentration profiles are shown in Fig. 4 for various times after the initial time t = 0, with x = distance along bed. You may assume that $c(L,t) = 0$ for $t \leq 2h$. Details of the experiment are as follows:

$u_o$ = superficial gas velocity = 13.1 cm/s;

$y_o$ = water mole fraction in entering gas = $5210 \times 10^{-6}$;

T = 20°C;

P = 3.0 atm;

$\rho_{bed}$ = 0.30 g silica gel/$cm^3$ bed volume

The break-point time $t_b$ is defined by the criterion $c(L,t_b) = 0.10\ c_o$.

Elroy abandoned the experiment after 5 hours (to go buy some bananas to eat). Thus, insufficient data exist to determine the saturation capacity of the bed by time integration. Figure 5 will allow you to determine $W_{sat}$ by alternate means.

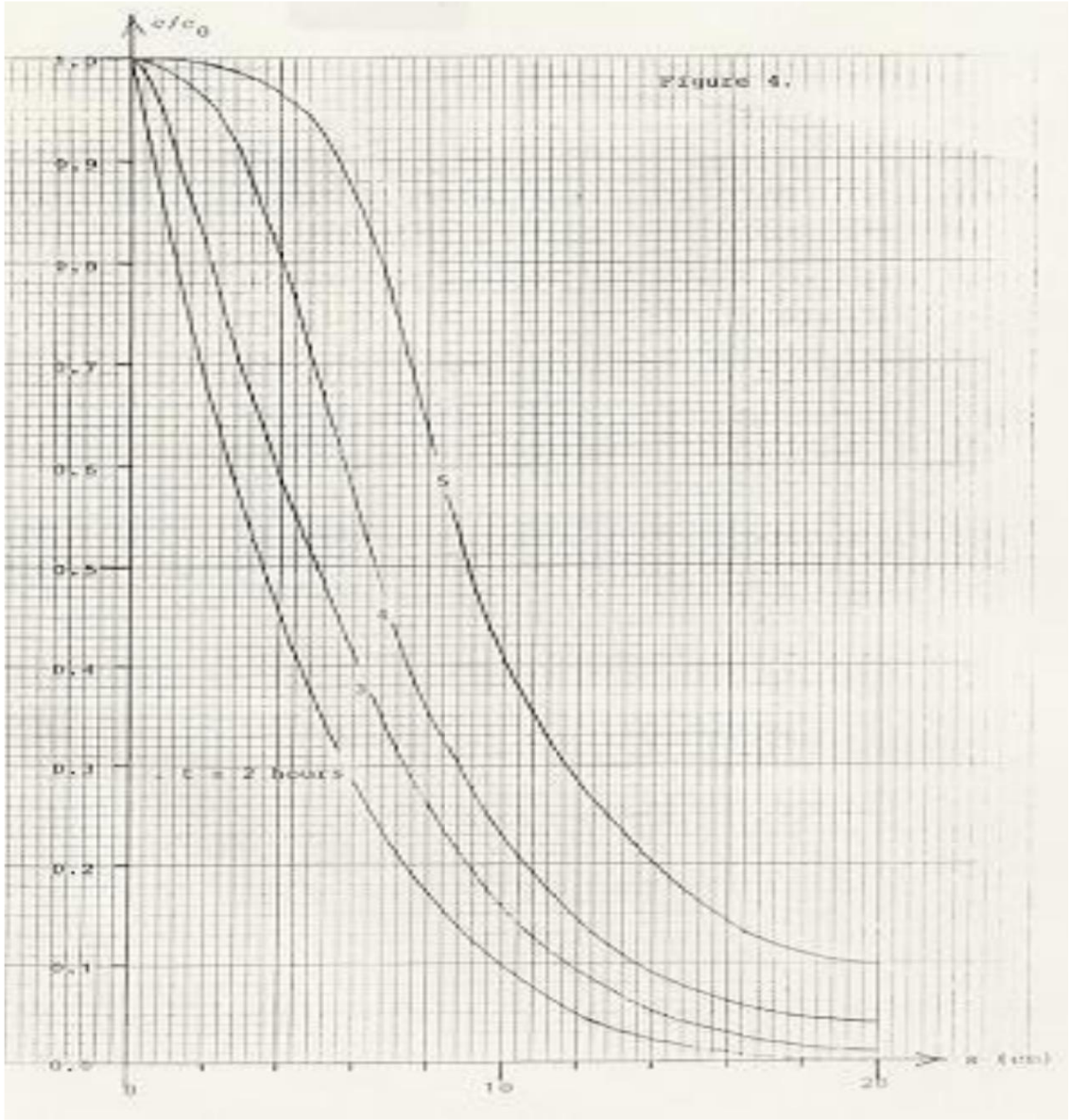
(a) (10 points) What is the saturation capacity of the bed $W_{sat}$ in g water/g silica gel?

(b) (30 points) What is the unused capacity of the silica gel (in terms of equivalent bed length) at the break-point?

(c) (10 points) Estimate the break-point time for a longer bed length of 100 cm, all other conditions being equal.

Data: vapor pressure of water

| T(°C) | $P^{sat}_{H_2O}$ (mm Hg) |
|---|---|
| 20 | 19.8 |
| 30 | 31.8 |
| 40 | 55.3 |



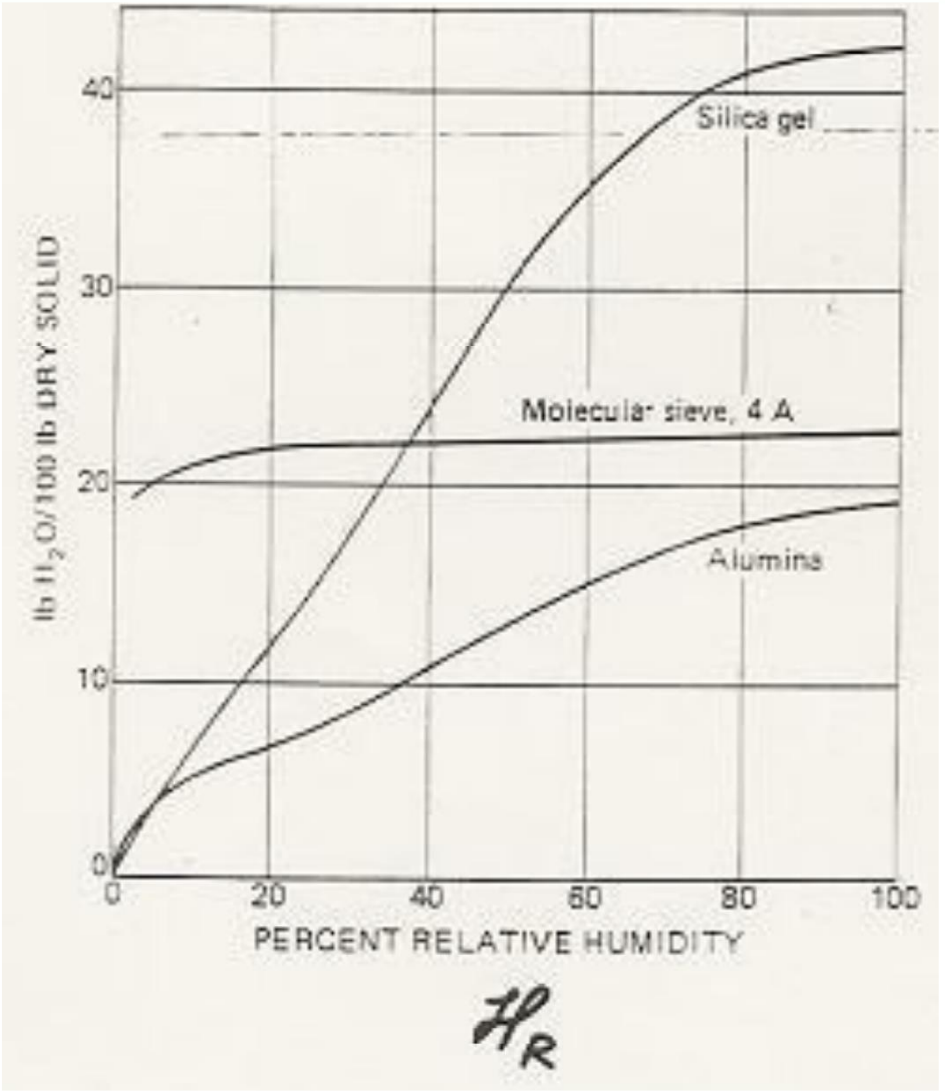




**Figure 24-3** Adsorption isotherms for water in air at 20 to 50°C.

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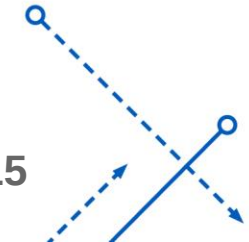
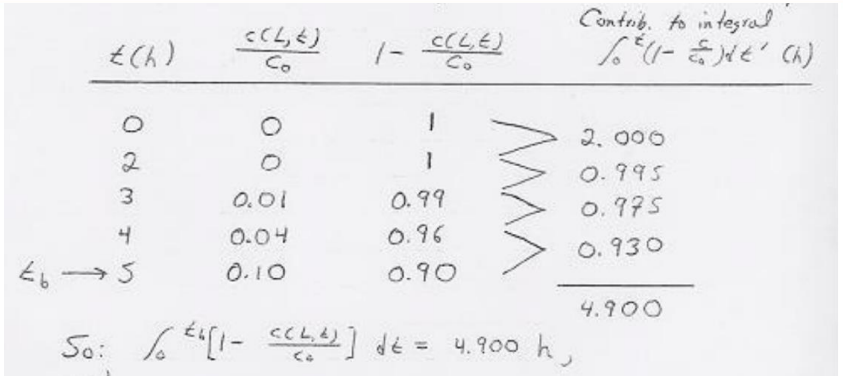


$$w(t) = \frac{\int_0^t F_{A\,in}\left(1 - \frac{c}{c_0}\right) dt}{L\,\rho_{bed}}$$

$$\frac{w_b}{w_{sat}} = \textit{fraction of bed utilized}$$



(c)

$$t_{b\,2}/t_{b\,1} = \frac{L_2 * \left(1 - \frac{LUB}{L_2}\right)}{L_1 * \left(1 - \frac{LUB}{L_1}\right)}$$

This problem deals with some experiments performed in Elroy Hutch's laboratory on adsorption of n-hexanol from air in a 10 cm long carbon-filled bed. Measured concentration profiles are shown in Fig. 1 for various times after the initial time t = 0, with x = distance along bed.

Details of the experiment are as follows:

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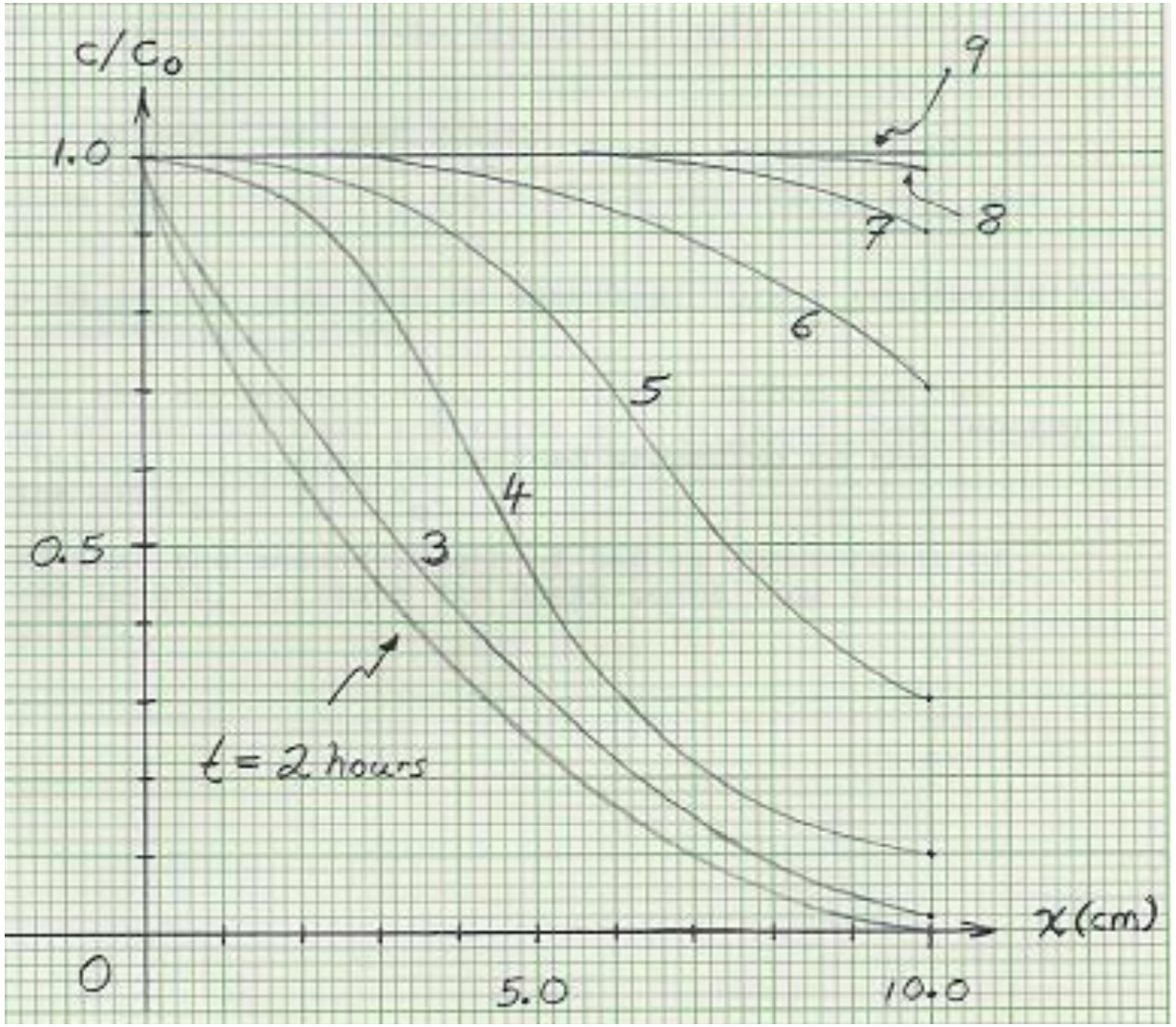
You may assume that $c(L,t) = 0$ for $t \leq 2$ h and $c(L,t) = c_o$ for for $t \geq 9$ h.

(a) Prepare in either graphical or numerical form a representation of the breakthrough curve.

(b) Calculate the saturation capacity of the carbon and the fraction of the bed used (in terms of equivalent bed length) at the beakpoint if this is defined according to the criterion $c(L,t_b) = 0.10\ c_o$.

(c) Assuming that the unused length of bed is independent of total bed length, estimate the break-point time for a 20 cm long bed.

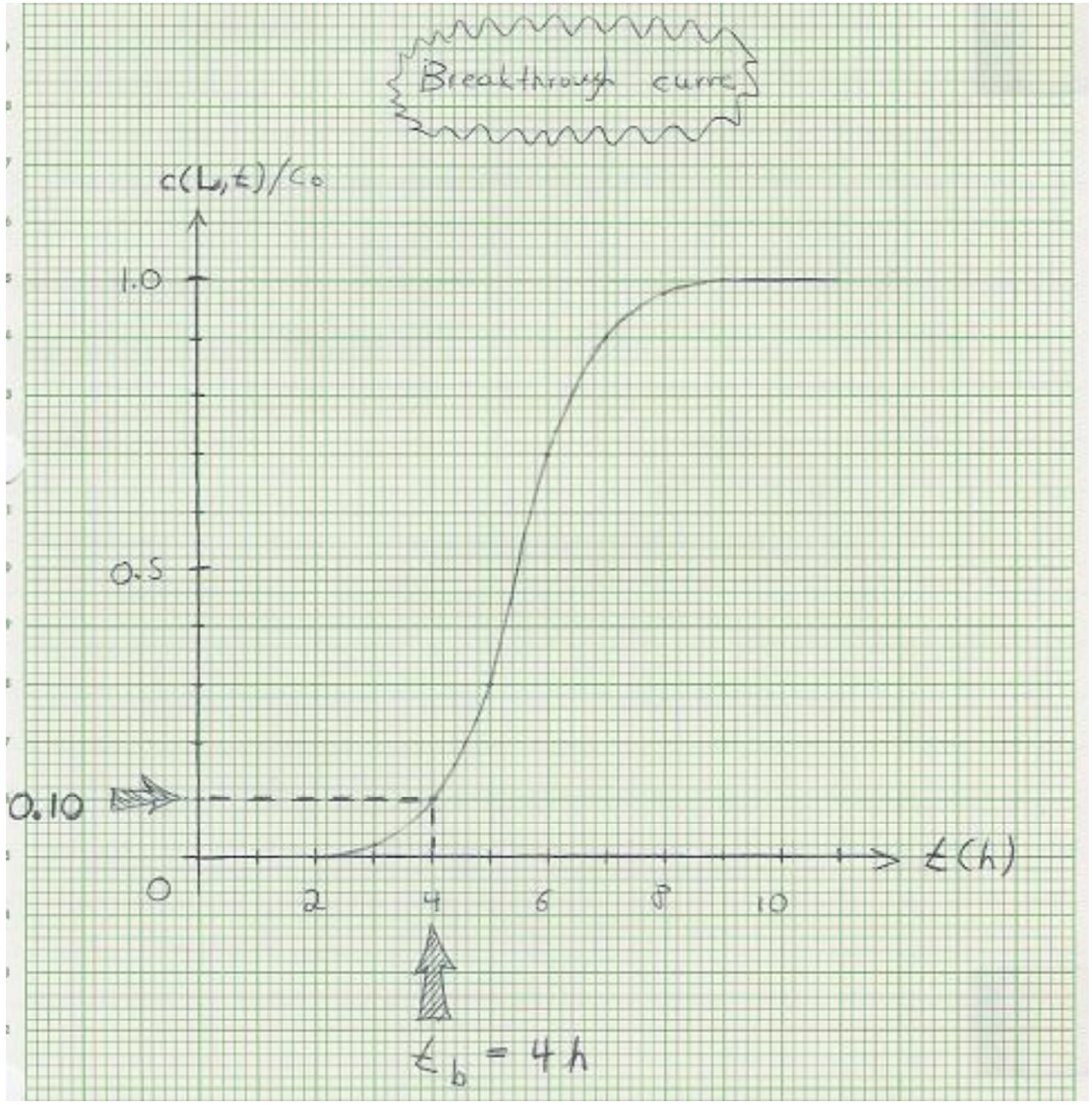



total bed length, 10 cm

(a) Breakthrough curve is $c(L,t)/c_0$ plotted as function of time. From graph provided (Fig. 1), construct table.

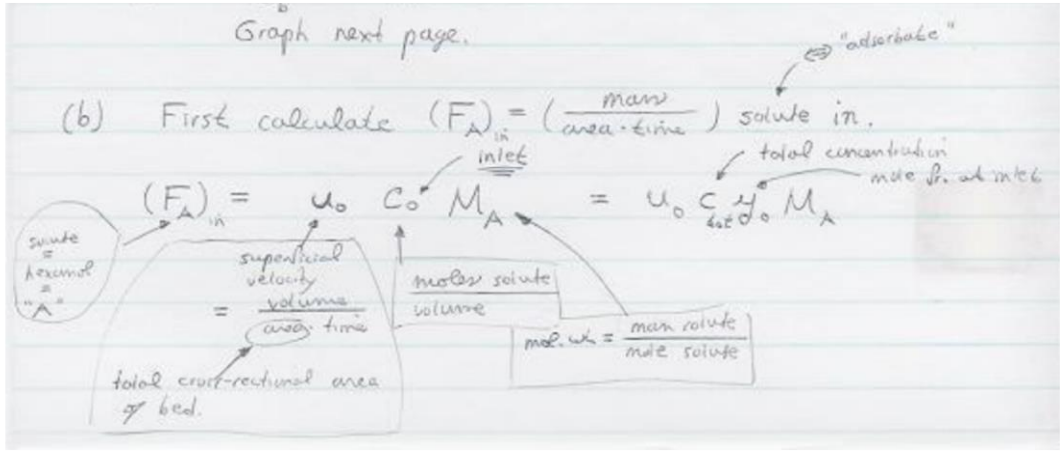
| $t$ (h) | $c(L,t)/c_0$ |
|---|---|
| 0 | 0 |
| 2 | 0 |
| 3 | 0.02 |
| 4 | 0.10 |
| 5 | 0.30 |
| 6 | 0.70 |
| 7 | 0.90 |
| 8 | 0.98 |
| 9 | 1 |
| (all later times | 1 ) |

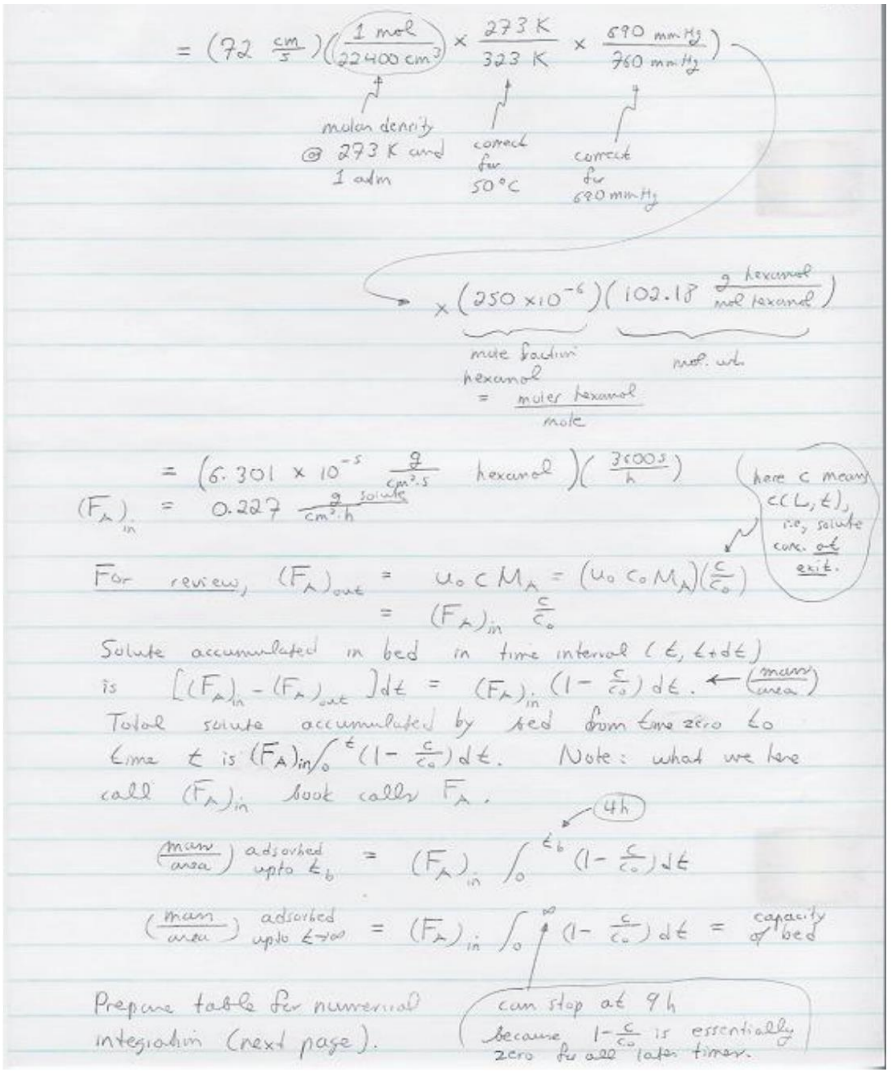
Note: breakpoint (time @ which $c(L,t)/c_0 = 0.10$) is $t_b = 4$ h.


Breakthrough curve
c(L,t)/c0
1.0
0.5
0.10
0
2
4
6
8
10
t(h)
tb = 4 h

$$w(t) = \frac{\int_0^t F_{A\,in}\left(1 - \frac{c}{c_0}\right) dt}{L\,\rho_{bed}}$$

$$\frac{w_b}{w_{sat}} = \textit{fraction of bed utilized}$$



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| $t$ (h) | $1 - \frac{c}{c_0}$ ($c(L,t)$) | contribution to integral $\int_0^t (1-\frac{c}{c_0})dt$ † (h) |
|---|---|---|
| 0 | 1 | 2 |
| 2 | 1 | 0.99 |
| 3 | 0.98 | 0.94 |
| 4 | 0.90 | 0.80 |
| 5 | 0.70 | 0.50 |
| 6 | 0.30 | 0.20 |
| 7 | 0.10 | 0.06 |
| 8 | 0.02 | 0.01 |
| 9 | 0 | |

upto breakpoint

$$\int_0^{t_b (4h)} \left(1 - \frac{c}{c_0}\right) dt = (2 + 0.99 + 0.94)h = 3.93\ h$$

$$\int_0^{\infty} \left(1 - \frac{c}{c_0}\right) dt = (3.93 + 0.80 + 0.50 + 0.20 + 0.06 + 0.01)h = 5.50\ h$$

$\left(\frac{\text{mass}}{\text{area}}\right)$ adsorbed upto $t_b$ $= \left(0.227 \frac{g}{cm^2 h}\right)(3.93\,h)$ solute

$\left(\frac{\text{mass}}{\text{area}}\right)$ adsorbed upto $t \to \infty$ $= \left(0.227 \frac{g}{cm^2 h}\right)(5.50\,h)$ solute

Capacity generally expressed in terms of $W$ $\left(\frac{\text{mass adsorbed}}{\text{mass adsorbent}}\right)$.

Know $\frac{\text{mass bed}}{\text{area}} = \frac{\text{vol. bed}}{\text{area}} \cdot \frac{\text{mass bed}}{\text{volume}} = L \rho_{bed}$

$= (10\ cm)\left(\frac{0.45\ g}{cm^3}\right) = 4.5 \frac{g\ carbon}{cm^2}$

† Use trapezoid rule, $\int_a^b f(x)dx \approx \frac{b-a}{2}[f(a) + f(b)]$, for each interval.

5

adsorbed upto breakpoint

$$W_b = \frac{\left(0.227 \frac{g}{cm^2 h}\right)(3.93\,h)\ \text{solute}}{4.5 \frac{g}{cm^2}\ \text{carbon}} = 0.198 \frac{g\ \text{solute}}{g\ \text{carbon}}$$

$$W_{sat} = \frac{\left(0.227 \frac{g}{cm^2 h}\right)(5.50\,h)\ \text{solute}}{4.5 \frac{g}{cm^2}\ \text{carbon}} = 0.277 \frac{g\ \text{solute}}{g\ \text{carbon}}$$

bed completely saturated

saturation capacity of the carbon

Fraction of bed capacity utilized at breakpoint $= W_b / W_{sat} = \frac{0.198}{0.277} = 0.715$ fr. bed capacity used at $t_b$

for 10 cm bed. Used length $= (0.715)(10\ cm) = 7.15\ cm$

Unused length $= 10 - 7.15 = 2.85\ cm$

equivalent unused length

equivalent used length

(c)

$$t_{b\,2}/t_{b\,1} = \frac{L_2 * \left(1 - \frac{LUB}{L_2}\right)}{L_1 * \left(1 - \frac{LUB}{L_1}\right)}$$

$t_{b\,1}$=4h; $L_2$ =20cm; $L_1$=10cm; $LUB$=2.85cm

$t_{b\,2}$=9.6h

This problem deals with some experiments performed in Elroy Hutch's laboratory on adsorption of water from air in a bed filled with silica gel (length L = 60 cm). Measured concentration profiles are shown in Fig. 4 for various times after the initial time t = 0, with x = distance along bed. You may assume that $c(L,t) = 0$ for $t \leq 2h$. Details of the experiment are as follows:

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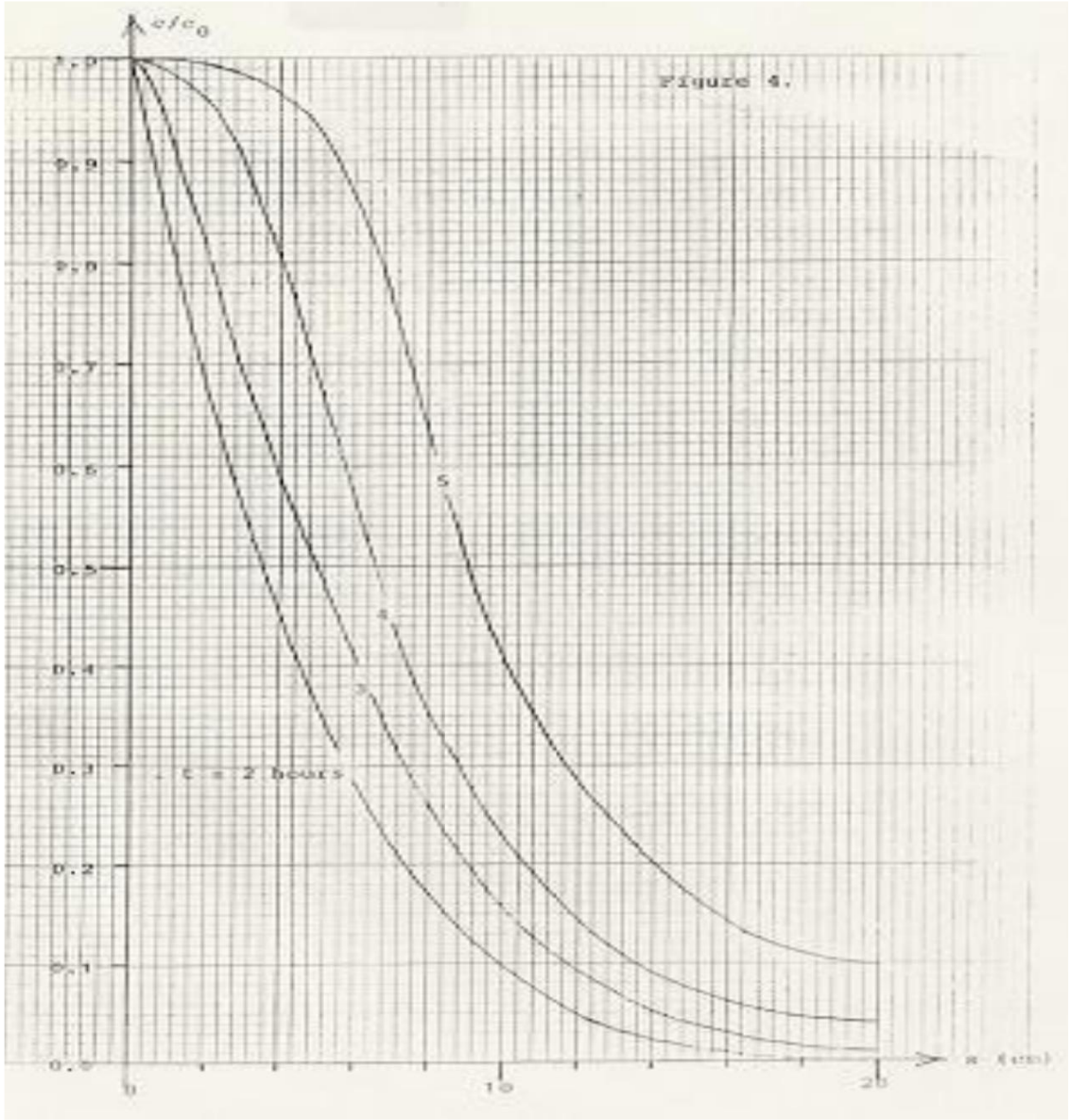


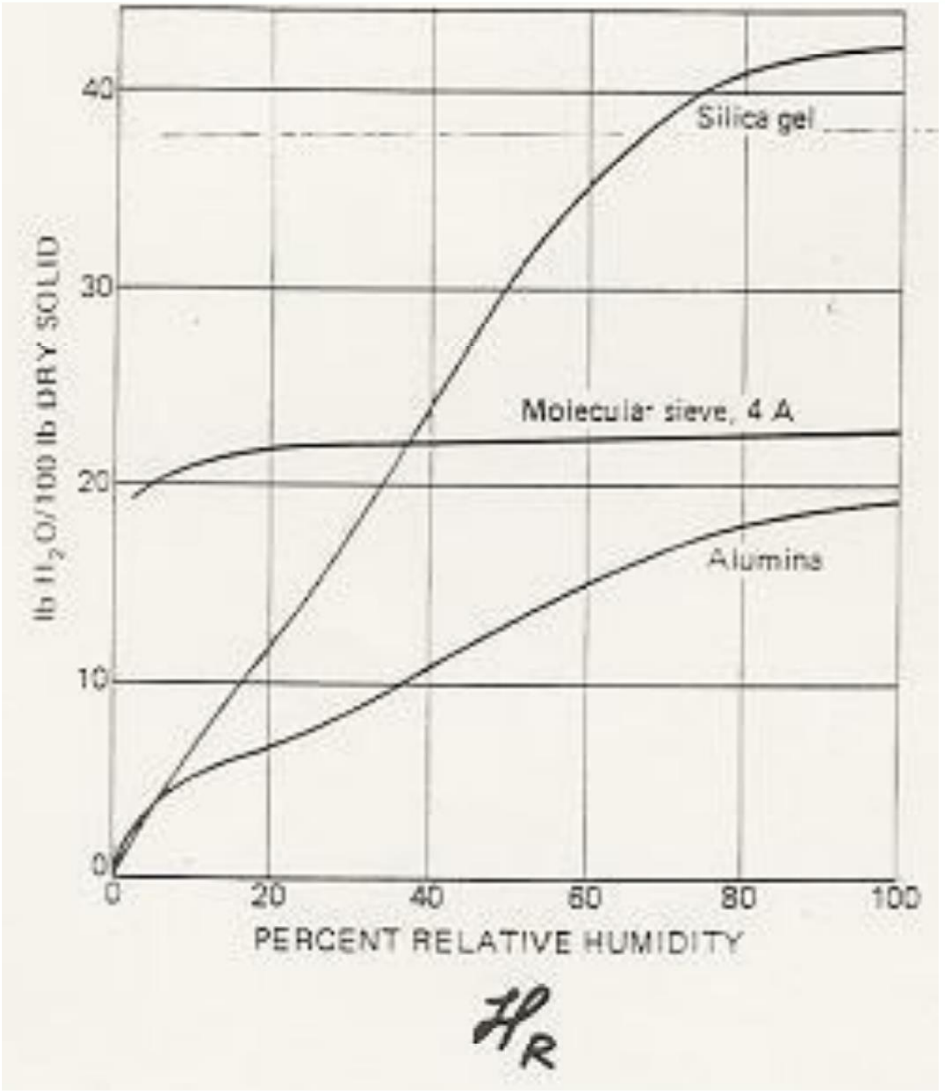




**Figure 24-3** Adsorption isotherms for water in air at 20 to 50°C.

(a) Incoming air: $p_{H_2O} = y_{H_2O} P$

$= (5210\ 10^{-6})(3\ \text{atm} \times \frac{760\ \text{mm Hg}}{1\ \text{atm}})$

$= 11.88\ \text{mm Hg}$

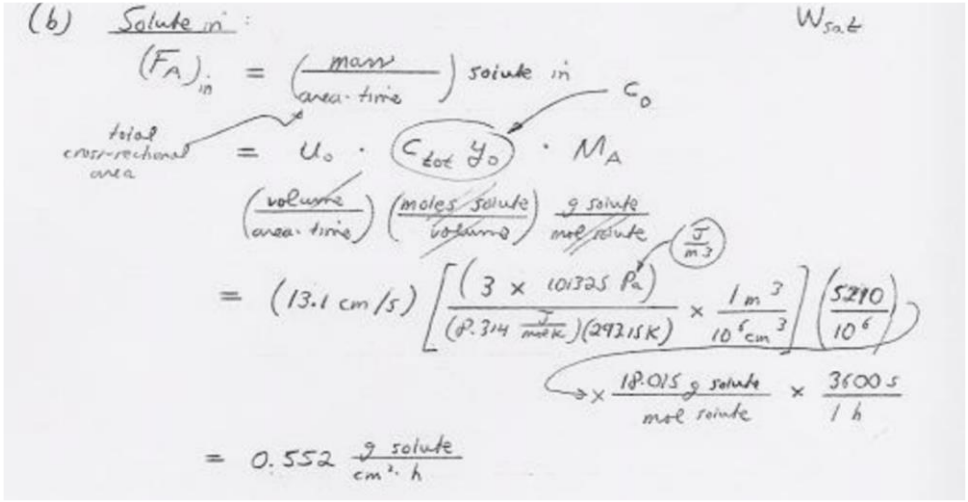
at 0°C $p^{sat}_{H_2O} = 19.8\ \text{mm Hg}$. Then

$H_R = (100\%)\frac{p_{H_2O}}{p^{sat}_{H_2O}} = (100\%)\frac{11.88}{19.8} = 60.0\ \%$

From Fig. 5, $W_{sat} = \frac{35.2\ \text{lb } H_2O}{100\ \text{lb silica gel}} = \boxed{0.352\ \frac{\text{g } H_2O}{\text{g silica gel}}}$

$$w(t) = \frac{\int_0^t F_{A\,in}\left(1 - \frac{c}{c_0}\right) dt}{L\,\rho_{bed}}$$

$$\frac{w_b}{w_{sat}} = \textit{fraction of bed utilized}$$



(b) Solute in: $W_{sat}$

$(F_A)_{in} = \left(\frac{\text{mass}}{\text{area}\cdot\text{time}}\right)$ solute in $= U_0 \cdot C_{tot}\, y_0 \cdot M_A$ ($C_0$; total cross-sectional area)

$\left(\frac{\text{volume}}{\text{area}\cdot\text{time}}\right)\left(\frac{\text{moles solute}}{\text{volume}}\right)\frac{\text{g solute}}{\text{mol solute}}$ ($\frac{J}{m^3}$)

$= (13.1\ cm/s)\left[\frac{(3 \times 101325\ Pa)}{(8.314\ \frac{J}{mol\,K})(298.15\ K)} \times \frac{1\ m^3}{10^6\ cm^3}\right]\left(\frac{5290}{10^6}\right)$

$\times \frac{18.015\ g\ solute}{mol\ solute} \times \frac{3600\ s}{1\ h}$

$= 0.552\ \frac{g\ solute}{cm^2 \cdot h}$

Read off value of $c(L,t)$ from graph. Prepare table. Break-point time $t_b$ is time at which $c(L,t_b) = 0.10\ c_0$, so $t_b = 5\ h$.

| $t$ (h) | $\frac{c(L,t)}{c_0}$ | $1 - \frac{c(L,t)}{c_0}$ | Contrib. to integral $\int_0^t (1 - \frac{c}{c_0})dt'$ (h) † |
|---|---|---|---|
| 0 | 0 | 1 | |
| 2 | 0 | 1 | 2.000 |
| 3 | 0.01 | 0.99 | 0.995 |
| 4 | 0.04 | 0.96 | 0.975 |
| $t_b \rightarrow$ 5 | 0.10 | 0.90 | 0.930 |
| | | | 4.900 |

So: $\int_0^{t_b}\left[1 - \frac{c(L,t)}{c_0}\right] dt = 4.900\ h$,

and

$\left(\frac{\text{mass solute}}{\text{area}}\right)$ adsorbed upto $t_b = (F_A)_{in}(4.900h)$

To get capacity in mass solute adsorbed / mass silica gel, use the fact that

$\left(\frac{\text{mass silica gel}}{\text{area}}\right) = \frac{\text{bed vol.}}{\text{bed area}} \cdot \frac{\text{mass silica gel}}{\text{bed vol.}}$

$= L\,\rho_{bed} = (60\ cm)(0.30\ \frac{g\ silica\ gel}{cm^3})$

$= 18.0\ \frac{g\ silica\ gel}{cm^2}$

Then $W_b = \frac{\text{mass adsorbed upto } t_b}{\text{mass silica gel}}$

† Use trapezoid rule, $\int_a^b f(x)dx \cong \frac{b-a}{2}[f(a) + f(b)]$, for each interval

$$= \frac{\text{mass adsorbed upto } t_b \text{ / area}}{\text{mass silica gel / area}}$$

$$W_b = \frac{(F_A)_{in}\,(4.900\ h)}{(L\,\rho_{bed})} = \frac{\left(0.352 \frac{g\ \text{solute}}{cm^2 \cdot h}\right)(4.900\ h)}{18.0 \frac{g\ \text{silica gel}}{cm^2}}$$

$$= 0.150 \frac{g\ \text{solute}}{g\ \text{silica gel}}$$

Fraction of bed capacity used at break-point

$= W_b / W_{sat} = 0.150 / 0.352 = 0.426$

for 60 cm bed. Used length $= (0.426)(60\ cm)$

$= 25.6\ cm$

Unused length $= (60 - 25.6)\ cm = 34.4\ cm$

Unused capacity of bed (in terms of equivalent bed length) at break-point is $l_{unused} = 34.4\ cm$

(c)

$$t_{b\,2}/t_{b\,1} = \frac{L_2 * \left(1 - \frac{LUB}{L_2}\right)}{L_1 * \left(1 - \frac{LUB}{L_1}\right)}$$

$t_{b\,1}$=5h; $L_2$ =100cm; $L_1$=60cm; $LUB$=34.4cm

$t_{b\,2}$= 12.8 h