

Problem Set # 8

3-14, 10, 23, 30, 37

Solutions

14.



$$\frac{dh}{dx} = 0.001 \text{ (N} \rightarrow \text{S)}$$

$$K = 10^{-4} \text{ m/s}$$

$$b = 10 \text{ m}$$

find necessary pumping rate to capture all the pollutant

using capture curves (p. 223):

- dumping area extends ~ 500 m to each side of well A

- this corresponds to $\frac{Q_w}{bq_a} \approx 1200 \text{ m}$ (assuming dispersion can be neglected)

$$q_a = K \frac{dh}{dx} = 10^{-4} \text{ m/s} (0.001) = 10^{-7} \text{ m/s}$$

$$Q_w = 1200 \text{ m} (bq_a)$$

$$= 1200 \text{ m} (10 \text{ m}) (10^{-7} \text{ m/s}) = \boxed{1.2 \times 10^{-3} \text{ m}^3/\text{s}}$$

16. a) saturated: $n = 0.3$, $f_{oc} = 1\%$, $\rho_b = 2.1 \text{ g/cm}^3$

CHCl_3 . $K_{ow} = 10^{1.97}$

estimate retardation factor

1st equation in table 3-5:

$$\log K_{oc} = 0.544 \log K_{ow} + 1.377$$

$$= 0.544 (1.97) + 1.377 = 2.45$$

$$K_d = f_{oc} K_{oc}$$

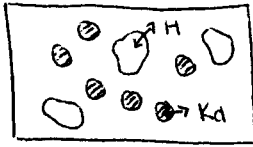
$$= 0.01 (10^{2.45} \text{ mL/g}) = 2.81 \text{ mL/g}$$

$$R = 1 + \frac{K_d \rho_b}{n} = 1 + \frac{(2.81 \text{ mL/g}) (2.1 \text{ g/cm}^3)}{0.3} = 20.7$$

$$\boxed{R \approx 21}$$

b) unsaturated: $\theta = 0.15$ (fraction of water)

Note that the equation given in lecture, $R = 1 + \frac{K_d \rho_b}{\theta}$, refers to a chemical that is not volatile.



CHCl_3 partitions into organic carbon according to K_d , and into the air according to H . Both of these phases are immobile.

go back to the most basic definition of R :

$$R = \frac{\text{mobile} + \text{immobile}}{\text{mobile}}$$

mobile - CHCl_3 in water

immobile - CHCl_3 in air, org. carbon

$$\text{amount in water} = C_w \cdot \theta$$

$$\text{amount in air} = C_a (n - \theta) \quad \leftarrow n \text{ includes air + water; } \theta \text{ is water only}$$

$$\text{amount in org. carbon} = C_s \cdot \rho_b$$

$$R = \frac{C_w \cdot \theta + C_a (n - \theta) + C_s \cdot \rho_b}{C_w \cdot \theta} = 1 + \frac{C_a (n - \theta)}{C_w \cdot \theta} + \frac{C_s \cdot \rho_b}{C_w \cdot \theta}$$

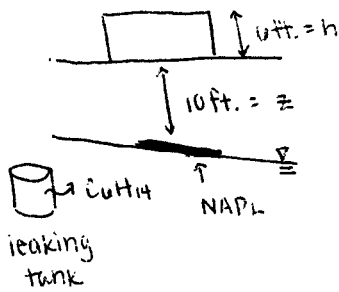
using the definitions that $H = \frac{C_a}{C_w}$ and $K_d = \frac{C_s}{C_w}$

$$\Rightarrow R = 1 + H \frac{(n - \theta)}{\theta} + \frac{K_d \cdot \rho_b}{\theta}$$

dimensionless

$$R = 1 + \frac{0.2(0.15)}{0.15} + \frac{2.81 \text{ mL/g} (2.1 \text{ g/cm}^3)}{0.15} = 40.5 \quad \boxed{R \approx 41}$$

23.

hexane: $MW = 86$ $P = 152 \text{ mmHg}$ (at 20°C)

$\rho = 0.66 \text{ g/cm}^3 \Rightarrow$ hexane is less dense than water;
 It will form a NAPL on top of
 the water table (and thus be
 diffusing through air)

a) for maximum flux:

- if hexane is directly under the compressor room

- if $C_{room} = 0$, and C_{air} (right above the NAPL) determined by vapor pressure

$$J = -D \frac{dc}{dx} \quad C_{air} = \frac{n}{V} = \frac{P}{RT} = \frac{152 \text{ mmHg} (1 \text{ atm} / 760 \text{ mmHg})}{.08206 \text{ L atm / mol K} (293 \text{ K})}$$

$$= .0083 \text{ mol/L} = 8.3 \text{ mol/m}^3$$

$$D_{eff} \approx D_a \cdot \frac{n}{\sqrt{2}} \quad \text{correction for porosity + tortuosity (p.231);}$$

other approximations are possible

$$= \frac{0.2 \text{ cm}^2/\text{s} (0.2)}{\sqrt{2}} = 0.028 \text{ cm}^2/\text{s}$$

$$J = 0.028 \frac{\text{cm}^2}{\text{s}} \cdot \left(\frac{\text{m}}{100 \text{ cm}}\right)^2 \times \frac{8.3 \text{ mol/m}^3 - 0}{3.048 \text{ m}} = \boxed{7.7 \times 10^{-6} \text{ mol/m}^2 \cdot \text{sec}}$$

b) We want to find C_{room} at steady state and compare this to the flammable limit.

at steady state, flux in = flux out

$$\text{flux in} = \frac{D_{eff} (C_{air} - C_{room})}{dx} = \frac{2.8 \times 10^{-6} \text{ m}^2/\text{s} (8.3 \text{ mol/m}^3 - C_{room})}{3.048 \text{ m}}$$

$$= 7.6 \times 10^{-6} \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} - 9.2 \times 10^{-7} \frac{\text{m}}{\text{s}} \cdot C_{room}$$

(multiply by area to get flux instead of flux density; taking $A = 1 \text{ m}^2$ is simplest)

flux out = volume · C_{room} · air changes (notice this is mol/time also)

for A = 1 m², V = 1.8 m³

$$(7.6 \times 10^{-4} \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} - 9.2 \times 10^{-7} \frac{\text{mol}}{\text{s}} \cdot C_{\text{room}}) (1 \text{ m}^2) = 1.8 \text{ m}^3 \cdot C_{\text{room}} \cdot \left(\frac{0.1}{\text{day}}\right) \times \frac{\text{d}}{86400 \text{ s}}$$

$$7.6 \times 10^{-4} - 9.2 \times 10^{-7} C_{\text{room}} = 2.1 \times 10^{-4} C_{\text{room}}$$

$$C_{\text{room}} = 2.5 \text{ mol/m}^3$$

Convert to partial pressure:

$$P = \frac{n}{V} RT = 2.5 \times 10^{-3} \text{ mol/L} \cdot (0.08206 \frac{\text{L atm}}{\text{mol K}}) (293 \text{ K}) = 0.061 \text{ atm}$$

Since ambient air pressure is 1 atm, the concentration of hexane is 6.1% ⇒ flammable limit is reached

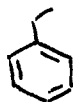
2b. 1.5 travel times have elapsed but the well is still pumping clean water... this means the contaminant has either been degraded or is being slowed down. Since BTEX are fairly hydrophobic (which means they have relatively high K_{ow} values) and the aquifer contains organic carbon, retardation is a definite possibility.



benzene



toluene



ethylbenzene



xylene

(3 arrangements possible)

for benzene, log K_{ow} = 2.13

Since these are aromatic compounds (aromatic = containing 6-carbon rings), we can use this equation:

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006 = 1.99$$

$$K_d = f_{oc} \cdot K_{oc} = 0.003 (10^{1.99}) = 0.293 \text{ mL/g}$$

$$R = 1 + \frac{K_d \rho_n}{n} = 1 + \frac{0.293 \text{ mL/g} (1.86 \text{ g/cm}^3)}{0.3} = 2.8$$

assume n = 0.3

$$\rho_b = (1-n) \rho_s$$

$$= 0.7 (2.65 \text{ g/cm}^3) = 1.86 \text{ g/cm}^3$$

Retardation can definitely account for the delay. The BTEX could also have been degraded, most likely through biodegradation (photolysis isn't going to be too likely underground, and aromatic compounds aren't really susceptible to hydrolysis).

- b) Biodegradation can account for the drop in pH. BTEX gets oxidized to CO_2 , which is acidic (as H_2CO_3).

initial

$$\text{pH} = 8$$

$$\text{Alk} = 5 \times 10^{-4} \text{ eq/L}$$

$$\Rightarrow C_T = 5 \times 10^{-4} \text{ M}$$

final

$$\text{pH} = 7$$

$$\text{Alk} = 5 \times 10^{-4} \text{ eq/L}$$

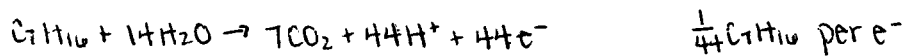
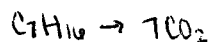
$$\Rightarrow C_T = 6 \times 10^{-4} \text{ M}$$

our good friend the
Deffeyes diagram...

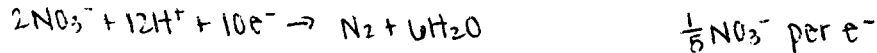
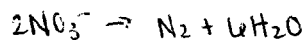
$$\Delta C_T \approx 10^{-4} \text{ M}$$

31. a) This is just a matter of balancing redox equations.

- assume complete oxidation to CO_2



- denitrification expected to occur: N_2 is product



$$25,000 \text{ g C}_7\text{H}_{16} \times \frac{\text{mol C}_7\text{H}_{16}}{100 \text{ g}} \times \frac{\frac{1}{5} \text{ mol NO}_3^-}{\frac{1}{44} \text{ mol C}_7\text{H}_{16}} \times \frac{1 \text{ mol NaNO}_3}{\text{mol NO}_3^-} \times \frac{85 \text{ g NaNO}_3}{\text{mol}}$$

$$= 187 \text{ kg NaNO}_3$$

- b) From p.136 we see that while denitrification is occurring, $p_e \approx 12$.