

## 1.725 Problem Set #4 Solutions

(Ch. 2 - 6, 11, 32, 47, 58)

6.

pentane:  $C_5H_{12}$ , 72 g/mol

octane:  $C_8H_{18}$ , 114 g/mol

a) pentane is removed according to  $C = C_0 e^{-K_r t}$

$$K_r = \frac{k}{\text{depth}} = \frac{1 \text{ cm/hr}}{400 \text{ cm}} = .0025 \text{ hr}^{-1}$$

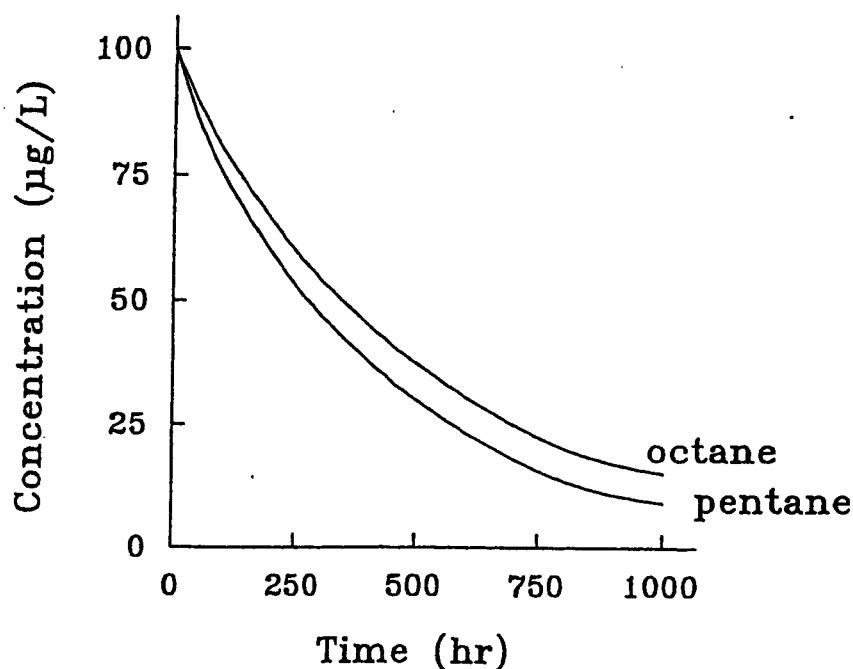
$$C = (100 \mu\text{g/L}) e^{-(.0025 \text{ hr}^{-1})t}$$

b) first, find  $K$  for octane (using thin film model since it's a lake)

$$\frac{k_0}{k_p} = \sqrt{\frac{M_w p}{M_w^0}} = \sqrt{\frac{72}{114}} = 0.795 \quad k_0 = 0.795 \text{ cm/hr}$$

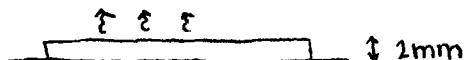
$$K_r = \frac{0.795 \text{ cm/hr}}{400 \text{ cm}} = .0020 \text{ hr}^{-1}$$

$$C = (100 \mu\text{g/L}) e^{-(.0020 \text{ hr}^{-1})t}$$



- c) Since pentane is volatilized more quickly (due to its lower molecular weight), over time the gasoline will contain a higher fraction of octane.
- d) biodegradation, sorption onto particles that settle to sediment, removal through a stream

11.



at air-NAPL interface:

$$C_a = \frac{P \text{ (MW)}}{RT} = \frac{(1013 \text{ mm Hg} \times 1 \text{ atm}) / (760 \text{ mm Hg})(91 \text{ g/mol})}{(0.08206 \text{ L atm/mol K})(293 \text{ K})} = 0.88 \text{ g/L}$$

$$k_a (\text{cm/hr}) \approx 1100 u_{10} (\text{m/s}) \\ = 3300 \text{ cm/hr}$$

$$J = k_a C_a = \frac{3300 \text{ cm}}{\text{hr}} \times \frac{0.88 \text{ g}}{\text{L}} \times \frac{\text{L}}{1000 \text{ cm}^3} = \frac{2.9 \text{ g}}{\text{cm}^2 \cdot \text{hr}}$$

taking an area of 1 cm<sup>2</sup> and finding the time for all the 1,2-dichloroethene to volatilize:

$$\text{volume} = 1 \text{ cm}^2 (0.2 \text{ cm}) = 0.2 \text{ cm}^3$$

$$0.2 \text{ cm}^3 \times \frac{1.28 \text{ g}}{\text{cm}^3} = 0.256 \text{ g}$$

$$\text{time} = \frac{0.256 \text{ g}}{2.9 \text{ g}} \times \frac{\text{hr}}{60 \text{ min}} = 5.3 \text{ min}$$

So 20 minutes after the spill, there is no more 1,2-dichloroethene on the road.

32.

a) toluene

92 g/mol

stream → surface renewal model

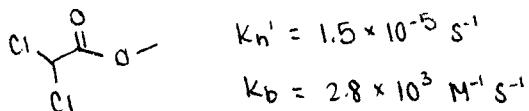
$$\frac{k_t}{k_p} = \sqrt{\frac{M W_p}{M W_t}} = \sqrt{\frac{44}{92}} = 0.832 \quad k_t = 0.832 (19 \text{ cm/hr}) = 15.8 \text{ cm/hr}$$

$$C_0 = \frac{9.0 \text{ mg/sec}}{3 \text{ L/sec}} = 3 \text{ mg/L}$$

$$K_r = \frac{K}{d} = \frac{15.8 \text{ cm/hr}}{20 \text{ cm}} = 0.79 \text{ hr}^{-1}$$

$$C = C_0 e^{-K_r t} = (3 \text{ mg/L}) e^{-0.79 \text{ hr}^{-1} (0.583 \text{ hr})} = 1.9 \text{ mg/L}$$

b) removed by hydrolysis rather than degassing, but same 1st-order approach:



$$K_t' = K_h' + K_b [\text{OH}^-] \quad \text{neglecting acid-catalyzed hydrolysis}$$

$$= 1.5 \times 10^{-5} \text{ s}^{-1} + 2.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} (10^{-6.5} \text{ M}) = 9.0 \times 10^{-4} \text{ s}^{-1}$$

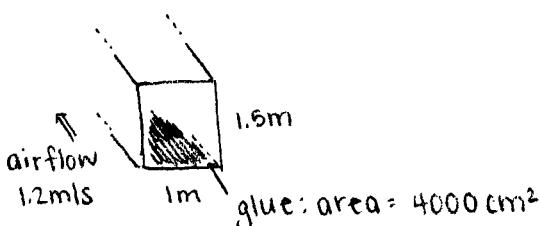
$$C = C_0 e^{-K_t' t} = (3 \text{ mg/L}) e^{-(9.0 \times 10^{-4} \text{ s}^{-1})(2100 \text{ s})} = 0.45 \text{ mg/L}$$

47.  $A_d = A_0 e^{-\lambda t} \Rightarrow t = -\frac{1}{\lambda} \ln \left( \frac{A_d}{A_0} \right)$

$$\lambda(^{210}\text{Pb}) = .03 \text{ yr}^{-1}$$

$$t = \frac{-1}{.03 \text{ yr}^{-1}} \ln \left( \frac{0.9}{3.4} \right) = 44 \text{ years}$$

58.



a)  $C_a = \frac{P}{RT} (\text{MW}) = \frac{10^{-2} \text{ atm} (92.14 \text{ g/mol})}{(0.08206 \text{ L atm/mol K})(298 \text{ K})} = 0.038 \text{ g/L}$

$$K_a = 1100 (1.2) = 1320 \text{ cm/hr}$$

$$J = K_a C_a = \frac{0.038 \text{ g}}{\text{L}} \times \frac{\text{L}}{1000 \text{ cm}^3} \times \frac{1320 \text{ cm}}{\text{hr}} = \frac{0.050 \text{ g}}{\text{cm}^2 \cdot \text{hr}}$$

over the whole surface:  $\frac{0.050 \text{ g}}{\text{cm}^2 \cdot \text{hr}} (4000 \text{ cm}^2) \times \frac{\text{hr}}{3600 \text{ s}} = 0.055 \text{ g/s}$

(amt. of toluene volatilized)

flow rate:  $Q = vA$

$$= (1.2 \text{ m/s})(1.5 \text{ m}^2) = 1.8 \text{ m}^3/\text{s}$$

Far downstream, the toluene is distributed evenly throughout the air duct.

$$C_{\text{tol}} = \frac{0.055 \text{ g/s}}{1.8 \text{ m}^3/\text{s}} \times \frac{\text{mol}}{92.14 \text{ g}} = \boxed{3.3 \times 10^{-4} \text{ mol/m}^3}$$

b)  $C_a = .038 \text{ g/L}$

$$k_a = 1100(2) = 2200 \text{ cm/hr} \quad \Rightarrow \quad J = .083 \text{ g/cm}^2 \cdot \text{hr}$$

$$\text{volatilization rate} = .092 \text{ g/s}$$

$$\text{flow rate} = 3 \text{ m}^3/\text{s}$$

$$\Rightarrow \boxed{C_{\text{tol}} = 3.3 \times 10^{-4} \text{ mol/m}^3}$$

The concentration is the same because the airflow velocity affects both the volatilization and flow rates.

c)

2 cm kitty litter

This is like the stagnant air layer in the thin film model; we are concerned with how much the toluene diffuses through the kitty litter, and how much kitty litter there is.

$$K = \frac{D}{L} = \frac{0.01 \text{ cm}^2/\text{s}}{2 \text{ cm}} = .005 \text{ cm/s}$$

now repeat previous calculations:

$$C_a = .038 \text{ g/L}$$

$$J = .038 \frac{\text{g}}{\text{L}} \times \frac{\text{L}}{1000 \text{ cm}^3} \times \frac{.005 \text{ cm}}{\text{s}} = 1.9 \times 10^{-7} \frac{\text{g}}{\text{cm}^2 \cdot \text{s}} (4000 \text{ cm}^3) = 7.6 \times 10^{-4} \text{ g/s}$$

$$C_{\text{tol}} = \frac{7.6 \times 10^{-4} \text{ g/s}}{1.8 \text{ m}^3/\text{s}} \times \frac{\text{mol}}{92.14 \text{ g}} = 4.6 \times 10^{-6} \text{ mol/m}^3, \text{ or } \boxed{72 \text{ times smaller}}$$

note: flux can also be calculated using  $J = -D \frac{dc}{dx}$ , taking  $c \approx 0$  at the top of the kitty litter.

(same numbers, slightly different thought process)