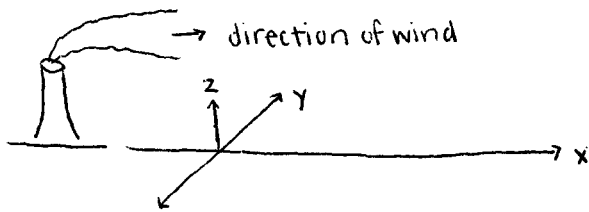


3.



$$Q = 10 \text{ kg/day}$$

$$h = 120 \text{ m}$$

$$u = 10 \text{ mi/hr}$$

$$C = \frac{Q}{u} \frac{g_1 g_2}{2\pi \sigma_y \sigma_z}$$

$$\frac{Q}{u} = \frac{10 \text{ kg}}{\text{day}} \times \frac{\text{hr}}{10 \text{ mi}} \times \frac{\text{day}}{24 \text{ hr}} \times \frac{\text{mi}}{1609 \text{ m}} = 2.59 \times 10^{-5} \text{ kg/m}$$

$$\text{along centerline, } y=0 \Rightarrow g_1 = e^{-0.5y^2/\sigma_y^2} = 1$$

at ground level, $z=0$

$$g_2 = e^{-0.5(z-H)^2/\sigma_z^2} + e^{-0.5(z+H)^2/\sigma_z^2}$$

$$= e^{-0.5H^2/\sigma_z^2} + e^{-0.5H^2/\sigma_z^2} = 2e^{-0.5H^2/\sigma_z^2}$$

$$C = \frac{(2.59 \times 10^{-5} \text{ kg/m})(2e^{-0.5(120\text{m})^2/\sigma_z^2})}{2\pi \sigma_y \sigma_z}$$

σ_y and σ_z are functions of x

using stability category B, urban conditions (residential areas)

$$\sigma_y = \frac{0.32x}{(1+0.0004x)^{0.5}}$$

$$\sigma_z = 0.24x(1+0.301x)^{0.5}$$

\Rightarrow substitute into above expression for C

b) $z=0$

$$x = 10 \text{ km} = 10,000 \text{ m}$$

$$y = 100 \text{ m}, 300 \text{ m}, 1000 \text{ m}$$

At ground level, 10 km downwind of the stack, how do zinc concentrations change as we move away from the centerline?

(\perp to direction of wind)

$$\sigma_y = \frac{0.32(10,000)}{(1+0.0004 \times 10,000)^{0.5}} = 1431 \text{ m}$$

$$\sigma_z = 0.24(10,000) \times (1+0.001 \times 10,000)^{0.5} = 7960 \text{ m}$$

find conc. at centerline ($y = 0, g_1 = 1$)

$$C = \frac{(2.59 \times 10^{-5} \text{ kg/m})}{2\pi} \frac{(2e^{-0.5(120\text{m})^2 / (17940\text{m})^2})}{(1431\text{m} \times 17940\text{m})} = 7.24 \times 10^{-13} \text{ kg/m}^3$$

When y changes, only g_1 is affected, so we can calculate g_1 at each y value and multiply it by this centerline concentration to get the actual concentration at each point.

$$g_1 = e^{-0.5y^2 / 16y^2}$$

$$\text{for } y = 100\text{m}, g_1 = e^{-0.5(100\text{m})^2 / (1431\text{m})^2} = 0.998$$

$$y = 300\text{m}, g_1 = 0.978$$

$$y = 1000\text{m}, g_1 = 0.783$$

⇒

$$\begin{aligned} C &= 7.2 \times 10^{-13} \text{ kg/m}^3 \\ C &= 7.1 \times 10^{-13} \text{ kg/m}^3 \\ C &= 5.7 \times 10^{-13} \text{ kg/m}^3 \end{aligned}$$

27. Since we are in a thunderstorm, the air is moist and the wet adiabatic lapse rate can be used. Hail will form at temperatures below 32°F, the freezing point of water.

Using figure 4-7 (the "skew T-log P" diagram):

- 1) start at the intersection of 68°F (diagonal) and 500 m (horizontal)
- 2) follow this adiabat (thick line sloping up to the left) until it crosses 32°F
- 3) this intersection corresponds to ~ 4500m

b) We can use Stokes' Law to find the settling velocity, which will give us some idea of the necessary updraft strength:

$$W_f = \frac{2}{9} \frac{g r^2 \Delta \rho}{\mu_f} \quad (\text{p. 354})$$

$$\mu_f = 1.83 \times 10^{-4} \text{ g/cm} \cdot \text{sec} \quad (\text{for } 18^\circ\text{C, which is not the case here...})$$

$$\Delta \rho \approx 1 \text{ g/cm}^3$$

$$g = 980 \text{ cm/s}^2$$

$$W_f = \frac{2}{9} \frac{(980 \text{ cm/s}^2)(0.05 \text{ cm})^2(1 \text{ g/cm}^3)}{1.83 \times 10^{-4} \text{ g/cm} \cdot \text{s}} = 2975 \text{ cm/s} \approx 30 \text{ m/s}$$

32.

$$k = 3 \times 10^{-15} \text{ cm}^3/\text{molec} \cdot \text{sec}$$

$$\text{assume } [\cdot\text{OH}] \approx 1 \times 10^6 \text{ molec}/\text{cm}^3$$

pseudo 1st order (which is valid when $[\cdot\text{OH}] \gg [\text{CH}_4]$, so reaction between the two basically doesn't affect $[\cdot\text{OH}]$):

$$k' = k[\cdot\text{OH}]$$

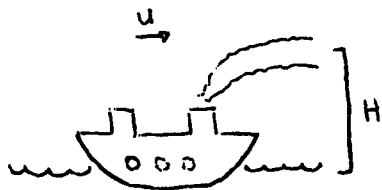
$$= 3 \times 10^{-15} \frac{\text{cm}^3}{\text{molec} \cdot \text{sec}} (10^6 \frac{\text{molec}}{\text{cm}^3}) = 3 \times 10^{-9} \text{ s}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{0.693}{3 \times 10^{-9} \text{ s}^{-1}} = 2.31 \times 10^8 \text{ s} = \boxed{7.3 \text{ years}}$$

We have also assumed that the troposphere is fairly well-mixed, so that $[\cdot\text{OH}]$ can be treated as being constant.

- b) Since $t_{1/2} \approx 8$ years for diffusion into the stratosphere, the loss processes occur at similar rates. This also means that methane oxidation due to $\cdot\text{OH}$ will lower tropospheric $[\text{CH}_4]$ significantly, decreasing flux to the stratosphere.

40.



"astern": behind ship

4000 L/hr hydrocarbons + chlorinated HC's

50 g/L chlorine content (as HCl)

$$H = 15 \text{ m}$$

$$u = 15 \text{ knots} \times \frac{1.15 \text{ mph}}{\text{knot}} = 17.25 \text{ mi/hr} = 7.7 \text{ m/s}$$

$$Q = \frac{4000 \text{ L}}{\text{hr}} \times \frac{50 \text{ g Cl}}{\text{L}} \times \frac{\text{mol Cl}}{35.45 \text{ g}} \times \frac{\text{mol HCl}}{\text{mol Cl}} = 5642 \text{ mol/hr}$$

night, $u = 7.7 \text{ m/s} \Rightarrow$ stability category D

using figure 4-25 we find:

$$\sigma_y = 17 \text{ m} \quad (\text{for } x = 200 \text{ m})$$

$$\sigma_z = 9 \text{ m}$$

$$\sigma_y = 75 \text{ m} \quad (x = 1000 \text{ m})$$

$$\sigma_z = 33 \text{ m}$$

$$C = \frac{Q}{u} \frac{g_1 g_2}{2\pi \sigma_y \sigma_z}$$

$$\frac{Q}{u} = \frac{5642 \text{ mol}}{\text{hr}} \times \frac{\text{sec}}{7.7 \text{ m}} \times \frac{\text{hr}}{3600 \text{ s}} = .207 \text{ mol/m}$$

$$y=0, \quad g_1 = \exp(-0.5 y^2 / \sigma_y^2) = e^0 = 1$$

$$z=0, \quad g_2 = \exp(-0.5 (z-H)^2 / \sigma_z^2) + \exp(-0.5 (z+H)^2 / \sigma_z^2) \\ = 2e^{-0.5 H^2 / \sigma_z^2}$$

$$c(200\text{m}) = \frac{.20\text{mol}}{\text{m}} \frac{(2e^{-0.5}(15\text{m})^2(19\text{m})^2)}{2\pi(17\text{m})(9\text{m})} = \boxed{1.1 \times 10^{-4} \text{ mol/m}^3}$$

$$c(1000\text{m}) = \frac{.20\text{mol}}{\text{m}} \frac{(2e^{-0.5}(15\text{m})^2(135\text{m})^2)}{2\pi(175\text{m})(35\text{m})} = \boxed{2.4 \times 10^{-5} \text{ mol/m}^3}$$

$$b) 3\text{ppm} = \frac{3\text{mg}}{\text{L}} \times \frac{\text{g}}{1000\text{mg}} \times \frac{\text{mol}}{36.46\text{g}} = 8.23 \times 10^{-5} \text{ mol/L HCl}$$

raindrops.

$$\frac{[\text{CO}_2]}{p\text{CO}_2} = \frac{10^{-1.5} \text{ M}}{\text{atm}} \quad p\text{CO}_2 \approx 10^{-3.5} \text{ atm}$$

$$[\text{CO}_2] = \frac{10^{-1.5} \text{ M}}{\text{atm}} \times 10^{-3.5} \text{ atm} = 10^{-5} \text{ M}$$

Assume this is C_T (in other words, pH will be low enough that HCO_3^- and CO_3^{2-} are negligible)

$$\text{Alk} = C_B - C_A = -[\text{HCl}] = -8 \times 10^{-5} \text{ eq/L}$$

$$\text{using Deffeyes diagram} \Rightarrow \boxed{\text{pH} \approx 4.1}$$

(Note: Alkalinity is also referred to as "acid neutralizing capacity" - the higher Alk is, the more effective the carbonate system is as a buffer against added acid. At low Alk there is no buffering effect, which is why ignoring CO_2 species entirely and calculating $\text{pH} = -\log[\text{H}^+]$ from HCl conc. gives the same answer.)

seawater:

$$\text{pH} = 8$$

$$C_T = 5 \times 10^{-4} \text{ M} \quad (\text{initial})$$

$$\Rightarrow \text{Alk} = 4.8 \times 10^{-4} \text{ eq/L}$$

$$\Delta \text{Alk} = \Delta(C_B - C_A) = -8 \times 10^{-5} \text{ eq/L}$$

$$\text{so Alk (final)} = 4 \times 10^{-4} \text{ eq/L}$$

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

(unchanged b/c re-equilibration is slow)

$$\Rightarrow \boxed{\text{pH} \approx 6.9}$$

42. a) in lake, removal is due to air-water exchange

$$k_r = \frac{k}{d} = \frac{0.5 \text{ m/d}}{3 \text{ m}} = 0.167 \text{ d}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k_r} = \frac{0.693}{0.167 \text{ d}^{-1}} = \boxed{4.2 \text{ days}}$$

Note: This assumes $[\text{TCE}]_{\text{air}} \approx 0$ (see below for full explanation), which would be valid if atmospheric reaction with $\cdot\text{OH}$ is very fast or if TCE were being removed from the lake area by wind.

b) In atmosphere, removal is due to attack by $\cdot\text{OH}$

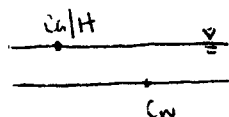
$$k' = k[\cdot\text{OH}]$$

$$= 2.4 \times 10^{-12} \frac{\text{cm}^3}{\text{molec} \cdot \text{sec}} \left(10^9 \frac{\text{molec}}{\text{cm}^3} \right) = 2.4 \times 10^{-6} \text{ sec}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k'} = 2.89 \times 10^5 \text{ sec} = \boxed{3.3 \text{ days}}$$

Explanation.

$$J = k(c_w - c_a/H)$$



waterside control

k is "piston velocity", $[L/T]$

Assuming $c_a \approx 0$, then $J = k c_w$.

If this is the only process that causes TCE removal, then

$$\frac{dM_w}{dt} = -k c_w A \quad \text{where } A \text{ is lake area} \quad (1)$$

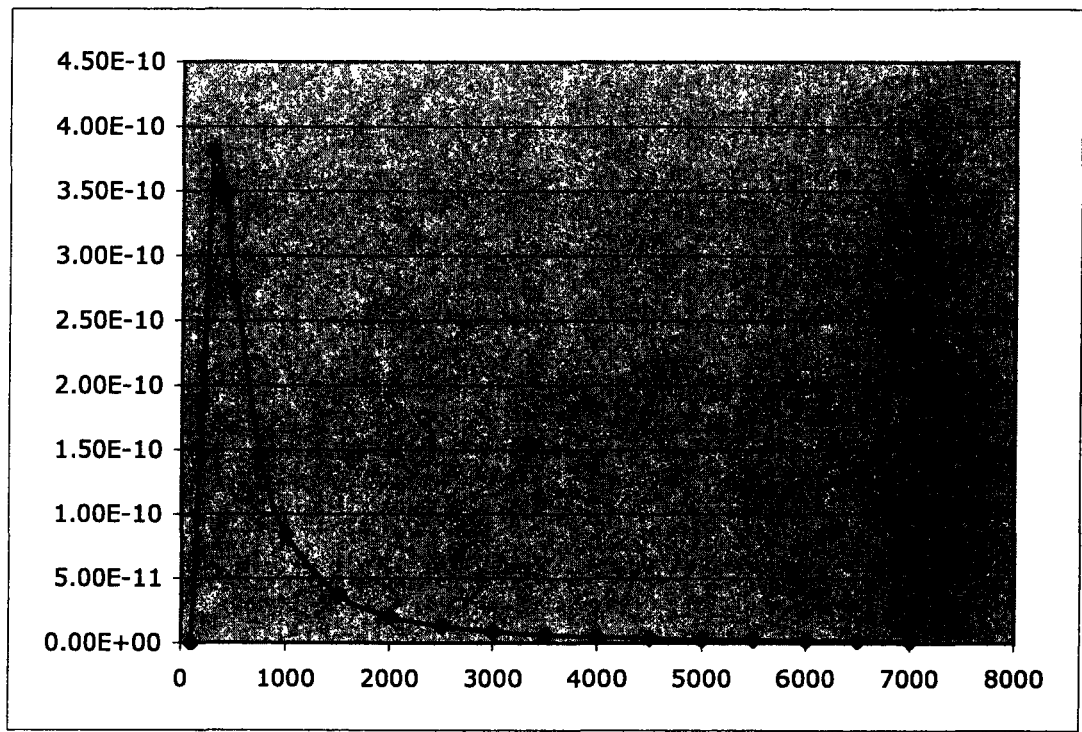
Rearranging the left side:

$$\frac{dM_w}{dt} = v \frac{dc_w}{dt} = A h \frac{dc_w}{dt} \quad \text{where } h \text{ is depth} \quad (2)$$

Setting (1) and (2) equal:

$$\frac{dc_w}{dt} = -\frac{k}{h} c_w \Rightarrow \text{first-order decay with a rate constant of } k/h \text{ [T}^{-1}\text{]}$$

x	sigma z	sigma y	g2	C
100	25	31	0.000	1.21E-13
200	53	62	0.148	1.88E-10
300	82	91	0.687	3.81E-10
400	114	119	1.145	3.50E-10
500	147	146	1.433	2.75E-10
750	238	210	1.761	1.45E-10
1000	339	270	1.879	8.44E-11
1500	569	379	1.956	3.73E-11
2000	831	477	1.979	2.06E-11
2500	1122	566	1.989	1.29E-11
3000	1440	647	1.993	8.82E-12
3500	1782	723	1.995	6.39E-12
4000	2147	794	1.997	4.83E-12
4500	2533	861	1.998	3.78E-12
5000	2939	924	1.998	3.04E-12
5500	3365	984	1.999	2.49E-12
6000	3810	1041	1.999	2.08E-12
6500	4272	1096	1.999	1.76E-12
7000	4752	1149	1.999	1.51E-12



for #3-a: this is the result when you plot the expression at various values of x. At first the concentration is low because the plume hasn't spread vertically enough to "hit" the ground. The decay at high values of x makes sense because the plume continues to spread out as it travels downwind.