

1.725 Quiz Solutions

1. a) Volume of rain = (15m)(1m)(0.05m) = 0.75 m³ = 750 L
 (0.1kg salt/750L)*(26 μmol Na₄Fe(CN)₆/kg salt) = 3.5*10⁻⁹ M Na₄Fe(CN)₆

b) [CN_T] = [HCN] + [CN⁻] (we are considering after photolysis)
 from mass action, [H⁺][CN⁻]/[HCN] = 10⁻⁹
 plug in pH 6.9, which gives [CN⁻]/[HCN] = 10^{-2.1} = .0079
 fraction = .0079/(1+.0079) = .008

c) Initial flux density is given by J = -k*C_{initial}
 Assuming complete photolysis, and knowing that most of the CN_T is present as HCN (from part b),
 [HCN] = 5[Na₄Fe(CN)₆] = 1.7*10⁻⁸ M.
 J = (1 cm/hr)(1.7*10⁻⁸ mol/1000 cm³) = 1.7*10⁻¹¹ mol/cm²hr
 (note that the puddle depth is an unnecessary piece of information)

2. a) definition of Henry's constant: H = C_{air}/C_{water}
 C_w = C_a/H = (0.2 atm)/(540 L atm mol⁻¹) = 3.7*10⁻⁴ mol/L

b) The system is at steady state, so flux in = flux out. Specifically, the rate of O₂ production via photosynthesis equals the rate of O₂ removal through air-water exchange.

In variables: J_{photo} = k_w([O₂]_{ss} - [O₂]_{equil})

Air-water exchange will be water-side controlled (can either recognize that O₂ is 20% of air, so it will be limited by the water, or calculate dimensionless H = 22 > 10⁻²).

k_w = 4*10⁻⁴ + 4*10⁻⁵(u₁₀)² = 4*10⁻⁴ cm/s

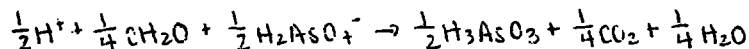
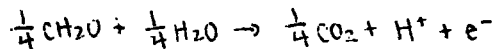
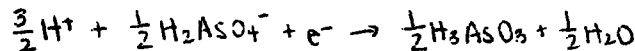
([O₂]_{ss} - [O₂]_{equil}) = J_{photo}/k_w = (.005 mol hr⁻¹ m⁻²)/(4*10⁻⁴ cm/s) = 3.5*10⁻⁴ M

we know [O₂]_{equil} from part a, giving [O₂]_{ss} = 7.2*10⁻⁴ M

c) only thing that changes is k_w = 4*10⁻⁴ + 4*10⁻⁵(2.5)² = 6.5*10⁻⁴ cm/s
 ([O₂]_{ss} - [O₂]_{equil}) = 2.1*10⁻⁴ M, so [O₂]_{ss} = 5.8*10⁻⁴ M

3. a) using H₂O to balance oxygen and H⁺ to balance hydrogen:
 CH₂O + H₂O → CO₂ + 4H⁺ + 4e⁻

b) express both reactions in terms of 1e⁻ and add together:



c) The arsenic reaction has a lower ΔG°, so it is more favorable. (Bonus points for the more accurate answer that it's actually ΔG that is compared, so we would have to know the concentrations to know for sure.)

d) mass action: $\frac{[\text{H}_3\text{AsO}_3]^{1/2}}{\{e^-\}[\text{H}^+]^{3/2}[\text{H}_2\text{AsO}_4^-]^{1/2}} = 10^{10.84}$
 $\{e^-\} = 1/(K[\text{H}^+]^{3/2}) = 10^{-0.34}$, pe = 0.34

4. a) Electroneutrality: $2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] = [\text{HCO}_3^-] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{Cl}^-]$
 $2(11 \text{ g/L} \cdot \text{mol}/40\text{g}) + 2(0.18 \text{ g/L} \cdot \text{mol}/24\text{g}) + (0.006 \text{ g/L} \cdot \text{mol}/23\text{g}) + (0.0012 \text{ g/L} \cdot \text{mol}/39\text{g})$
 $= 7.3 \cdot 10^{-3} \text{ mol/L of positive charges}$

similar calculation for anions yields $7.3 \cdot 10^{-3} \text{ mol/L of negative charges}$

Charges balance, so there is no evidence any charged species have been left out or misanalyzed.

b) use Henry's constant to find $[\text{H}_2\text{CO}_3]$ in equilibrium with atmosphere

$$K_H = [\text{H}_2\text{CO}_3]/p\text{CO}_2 = 10^{-1.5} \text{ mol L}^{-1} \text{ atm}^{-1}, p\text{CO}_2 = 10^{-3.5} \text{ atm}$$

$$[\text{H}_2\text{CO}_3] = 10^{-5} \text{ M}$$

$$\text{from the label, } [\text{HCO}_3^-] = (0.394 \text{ g/L})(\text{mol}/61 \text{ g}) = 6.5 \cdot 10^{-3} \text{ M}$$

now use mass action to find pH:

$$[\text{HCO}_3^-][\text{H}^+]/[\text{H}_2\text{CO}_3] = 10^{-6.3}, \text{ so } [\text{H}^+] = 7.8 \cdot 10^{-10} \text{ and pH} = 9.1$$

Alternatively, Alk can be calculated from the concentrations in part a (it will work out to $\text{Alk} = [\text{HCO}_3^-]$). You could then assume a pH of 8-9 so that HCO_3^- is the dominant species of C_T , and use the Deffeyes diagram to find pH (and then check that your assumption is correct).

c) At pH 9.1, $[\text{CO}_3^{2-}] = 4.1 \cdot 10^{-4} \text{ M}$ (from mass action, $K = 10^{-10.3}$)

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 6.9 \cdot 10^{-3} \text{ M}$$

Using Deffeyes, this corresponds to $\text{Alk} = 6.1 \cdot 10^{-3} \text{ eq/L}$ or so. Then C_T is doubled, and alkalinity doesn't change, resulting in a pH of about 6.4.

5. a) only consider volatilization, so $C = C_0 e^{-kt}$

$$k_{\text{benz}} = k_{\text{Ar}} \sqrt{(\text{MW}_{\text{Ar}}/\text{MW}_{\text{B}})} = 111 \text{ cm/hr (or 4th root, for surface renewal)}$$

$$\text{need rate constant with units of time}^{-1}: k = (111 \text{ cm/hr})/30 \text{ cm} = 3.7 \text{ hr}^{-1}$$

$$t = L/u = (800 \text{ m})/(50 \text{ cm/s}) = 1600\text{s} = 0.44 \text{ hr}$$

$$C = (3.85 \text{ ppm}) \exp(-3.7 \text{ hr}^{-1} \cdot 0.44 \text{ hr}) = 0.74 \text{ ppm} = 0.74 \text{ mg/L}$$

b) average = 0.653 (ppm)

$$\text{rearrange exponential decay equation: } k = \ln(C_0/C)/t = \ln(3.85/0.653)/0.44\text{hr} = 4.0 \text{ hr}^{-1}$$

c) Since the observed decay rate is larger than that predicted for volatilization, maybe some other process is removing the benzene. Or, since the rates are fairly close, maybe the observed rate is within the uncertainty limits of our predicted rate.

6. a) D_L is the longitudinal diffusion coefficient, which tells us how quickly a chemical spreads in the direction of river flow. This can be estimated from river characteristics:

$$D_L = 0.011 v^2 w^2 / d u^* \quad (v: \text{velocity, } w: \text{width, } d: \text{depth, all given in problem 5)}$$

$$u^* = \sqrt{g d s} = \sqrt{(9.8 \text{ m/s}^2)(0.3 \text{ m})(5 \cdot 10^{-4})} = 0.038 \text{ m/s}$$

$$v = 0.5 \text{ m/s, } w = 4 \text{ m, } d = 0.3 \text{ m gives } D_L = 3.9 \text{ m}^2/\text{s}$$

b) center of mass moves at the same velocity as the water, so $t = 1600\text{s}$ (from problem 5)

We are looking for how wide the cloud will be along the river, so $\sigma = \sqrt{2D_L t}$.

$$\sigma = \sqrt{2(3.9 \text{ m}^2/\text{s})(1600\text{s})} = 110 \text{ m}$$

$L = 4\sigma = 440 \text{ m}$ (this is 2σ away from the peak concentration in both directions, and encompasses 95% of the mass)