

## Problem Set 3—Key

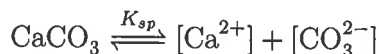
CENG 340—Introduction to Environmental Engineering

Instructor: Deborah Sills

September 17, 2013

### Questions

1. (12 pt) Precipitation–Dissolution



$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-8.3}$$

Since equilibrium occurs at the **end point of a reaction**, we need to calculate the final concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . To do so, set up a RICE table. R(reaction), I(initial conditions), C(change), and E(equilibrium). But first need to convert initial concentrations from mg/L to mole/L:

$$[\text{Ca}^{2+}] = 50 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mole}}{40 \text{ g}} = 8.3 \times 10^{-4} \frac{\text{moles}}{\text{L}}$$

$$[\text{CO}_3^{2-}] = 50 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mole}}{60 \text{ g}} = 1.25 \times 10^{-3} \frac{\text{moles}}{\text{L}}$$

Table 1: Rice Diagram

Reaction	$\text{Ca}^{2+}$	$\text{CO}_3^{2-}$	$\text{CaCO}_3$
<b>Initial</b>	$8.3 \times 10^{-4} \frac{\text{mole}}{\text{L}}$	$1.25 \times 10^{-3} \frac{\text{mole}}{\text{L}}$	0
<b>Change</b>	-x	-x	x
<b>Equilibrium</b>	$(8.3 \times 10^{-4} - x) \frac{\text{mole}}{\text{L}}$	$(1.25 \times 10^{-3} - x) \frac{\text{mole}}{\text{L}}$	x

Now we can substitute the equilibrium concentrations into the above equation for  $K_{sp}$

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = (8.3 \times 10^{-4} - x) \times (1.25 \times 10^{-3} - x) = 10^{-8.3}$$

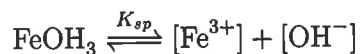
Solve for x.

$$x = 8.2 \times 10^{-4} \frac{\text{mole}}{\text{L}}$$

$$[\text{Ca}^{2+}]_{\text{equilibrium}} = 1.25 \times 10^{-3} - 8.2 \times 10^{-4} = 4.2 \times 10^{-4} \frac{\text{mole}}{\text{L}}$$

$$[\text{Ca}^{2+}]_{\text{equilibrium}} = 4.2 \times 10^{-4} \frac{\text{mole}}{\text{L}} \times \frac{40 \text{ g}}{\text{mole}} \times \frac{1000 \text{ mg}}{\text{g}} = 17 \frac{\text{mg}}{\text{L}}$$

2. (12 pt) Precipitation-Dissolution of Iron Hydroxide



$$\text{p}K_{sp} = 38.57$$

$$K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 10^{-38.57}$$

Equilibrium measures end-point of reaction, so need to use final iron concentration:

$$[\text{Fe}^{3+}] = 0.2 \frac{\text{mg}}{\text{L}}$$

$$[\text{Fe}^{3+}] = 0.2 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mole}}{56 \text{ g}} = 3.6 \times 10^{-6} \frac{\text{mole}}{\text{L}}$$

$$[\text{OH}^-] = \left( \frac{K_{sp}}{[\text{Fe}^{3+}]} \right)^{1/3} = \left( \frac{10^{-38.57}}{3.6 \times 10^{-6}} \right)^{1/3} = 9.1 \times 10^{-12} \frac{\text{mole}}{\text{L}}$$

$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} = \frac{10^{-14}}{9.1 \times 10^{-12}} = 0.001$$

$$\text{pH} = -\log(\text{H}^+) = 2.96$$

3. (12 pt) Calculate alkalinity in mg/L as  $\text{CaCO}_3$ :

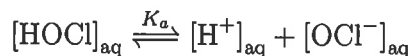
$$[\text{HCO}_3^-] = 111 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mole}}{61 \text{ g}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ eq}}{\text{mole}} = 1.8 \times 10^{-3} \frac{\text{eq}}{\text{L}} \text{ of alkalinity}$$

$$[\text{CO}_3^{2-}] = 17 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mole}}{60 \text{ g}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ eq}}{\text{mole}} = 5.7 \times 10^{-4} \frac{\text{eq}}{\text{L}} \text{ of alkalinity}$$

$$\text{Approximate Alkalinity (eq/L)} = 1.8 \times 10^{-3} + 5.7 \times 10^{-4} = 2.4 \times 10^{-3} \frac{\text{eq}}{\text{L}}$$

$$\text{Approximate Alkalinity (eq/L)} = 2.4 \times 10^{-3} \frac{\text{eq}}{\text{L}} \times \frac{100 \text{ g CaCO}_3}{\text{mole}} \times \frac{1 \text{ mole}}{2 \text{ eq}} = 119 \frac{\text{mg}}{\text{L}}$$

4. (12 pt) Acid-Base Equilibrium for HOCl in drinking water.  
Calculate fraction of HOCl that is in the dissociated form:



$$\text{p}K_a = 7.5$$

$$K_a = 10^{-7.5}$$

Since it's drinking water, assume  $\text{pH} = 7$ .

$$[\text{H}^+] = 10^{-7}$$

$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = 10^{-7.5}$$

Rearrange equation, and substitute values for  $K_a$  and  $[\text{H}^+]$ :

$$\frac{[\text{OCl}^-]}{[\text{HOCl}]} = \frac{10^{-7.5}}{10^{-7}}$$

$$[\text{OCl}^-] = 10^{-0.5} \times [\text{HOCl}] = 0.316[\text{HOCl}]$$

$$\text{FractionDissociated} = \frac{[\text{HOCl}]}{[\text{HOCl}] + [\text{OCl}^-]} = \frac{[\text{HOCl}]}{[\text{HOCl}] + 0.316[\text{HOCl}]} = \frac{1}{1 + 0.316} = 0.76$$

5. (12 pt) Atrazine in soil.

(a) This is a soil water partitioning problem governed by a linear isotherm:

$$q = K \times C$$

where  $q$  is the concentration of atrazine sorbed to the soil in units of  $\frac{\text{mg}}{\text{g soil}}$ ; and  $C$  is the dissolved or aqueous concentration of atrazine in units of  $\frac{\text{mg}}{\text{L}}$ ;  $K$  is the linear isotherm equilibrium constant in units of  $\frac{\text{L}}{\text{g}}$ .

$$K = 8 \times 10^{-3} \frac{\text{L}}{\text{g}}$$

(b) Draw a diagram.

(c) What do I need to report?:

*Soil + water contains  
Mass of  
Atrazine*

$$\text{Fraction of atrazine sorbed to soil} = \frac{\text{mass of sorbed atrazine}}{\text{mass of total atrazine}} =$$

$$= \frac{\text{mass of sorbed atrazine}}{\text{mass sorbed atrazine} + \text{mass dissolved atrazine}} =$$

$$= \frac{q \times \text{mass of soil}}{q \times \text{mass of soil} + C \times \text{volume of water}}$$

(d) What do I know:

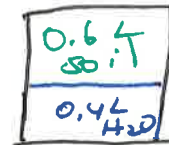
$$K = 8 \times 10^{-3} \frac{\text{L}}{\text{g}}$$

$$\rho_{\text{soil}} = 1.25 \frac{\text{g}}{\text{cm}^3} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} = 1250 \frac{\text{g}}{\text{L}}$$

$$\text{porosity} = 0.4 \frac{\text{vol voids}}{\text{vol total}}$$

$$\text{Saturation} = 100\%.$$

Thus in every 1 L of soil and water mixture, there are 0.4 L of water and 0.6 L of soil.  
In addition,



$$\text{mass of soil} = \text{volume of soil} \times \text{density of soil} = 0.6 \times \rho_{\text{soil}} = 0.6 \text{ L} \times 1250 \frac{\text{g}}{\text{L}} = 750 \text{ g}$$

(e) Go back and remind myself what I need to calculate:

$$\text{Fraction of atrazine sorbed} = \frac{q \times \text{mass soil}}{q \times \text{mass soil} + C \times \text{vol water}}$$

But for every liter of soil and water mix:

$$\text{Fraction of atrazine sorbed} = \frac{q \times 750 \text{ g}}{q \times 750 \text{ g} + C \times 0.4 \text{ L}}$$

In addition, I know from the sorption (equilibrium) expression that  $C = q/K$ , so

$$\text{Fraction of atrazine sorbed} = \frac{q \times 750 \text{ g}}{q \times 750 \text{ g} + \frac{q}{K} \times 0.4 \text{ L}}$$

$$\text{Fraction of atrazine sorbed} = \frac{q \times 750 \text{ g}}{q \times 750 \text{ g} + \frac{q}{8 \times 10^{-3} \frac{\text{L}}{\text{g}}} \times 0.4 \text{ L}}$$

$$\text{Fraction of atrazine sorbed} = \frac{750 \text{ g}}{750 \text{ g} + \frac{0.4 \text{ L}}{8 \times 10^{-3} \frac{\text{L}}{\text{g}}}} = 0.937$$

6. (15 pt) Oil Spill nineteen years ago:

$$C_0 = 400 \frac{\text{mg}}{\text{L}} \quad C \text{ after } 19\text{y} = 400 \frac{\text{mg}}{\text{L}}$$

(a) Try a zero order rate equation:

$$\frac{dC}{dt} = -k$$

After integration:

$$C = C_0 - kt$$

where  $C_0 = 400 \frac{\text{mg}}{\text{g}}$   
 $C = 20 \frac{\text{mg}}{\text{g}}$   
 $t = 19 \text{ year}$

Solve for  $k = 20 \text{ t}_{-1}$ , and substitute  $k$  into the integrated zero rate equation above to obtain

$$C = C_0 - 20 \text{ year}^{-1} \times 20 \text{ year} = 0$$

Answer: Yes the engineer is correct if the degradation rate is zero order.

- (b) To find the “worst-case scenario,” calculate the concentration of the pollutant after twenty years using a first order and second order rate equation.

**First Order:**

$$C = C_0 \times e^{-kt}$$

Solve for  $k$ :

$$k = -\frac{\ln \frac{C}{C_0}}{t} = -\frac{\ln \frac{20}{400}}{19 \text{ y}} = 0.16 \text{ y}^{-1}$$

Use  $k$  and solve for the time it will take to for  $C = 1 \frac{\text{mg}}{\text{kg}}$ , assuming first-order kinetics:

$$t = -\frac{\ln \frac{C}{C_0}}{k} = -\frac{\ln \frac{1}{400}}{0.16 \text{ year}^{-1}} = 37 \text{ y}$$

**Second Order:**

$$C = \frac{C_0}{1 + C_0 kt}$$

Rearrange and solve for  $k$ :

$$k = \frac{\frac{1}{C} - \frac{1}{C_0}}{t} = \frac{(\frac{1}{20} - \frac{1}{400}) \frac{\text{kg}}{\text{mg}}}{19 \text{ y}} = 0.003 \frac{\text{kg}}{\text{mg} \times \text{y}}$$

Use  $k$  and solve for the time it will take for  $C = 1 \frac{\text{mg}}{\text{kg}}$ , assuming second-order kinetics:

$$t = \frac{\frac{1}{C} - \frac{1}{C_0}}{k} = \frac{(\frac{1}{1} - \frac{1}{400}) \frac{\text{kg}}{\text{mg}}}{0.003 \frac{\text{kg}}{\text{mg} \times \text{y}}} = 333 \text{ y}$$

avg betw 333-400  
50k!

In conclusion the "worst-case scenario" is second order, in which case, it would take 399 y for the pollutant to degrade. However, first order is more likely.

#### 7. (12 pt) Volume Balance on Landfill

$$\text{Area of landfill} = 16.2 \text{ ha} \times \frac{10,000 \text{ m}^2}{\text{ha}} = 162,000 \text{ m}^2$$

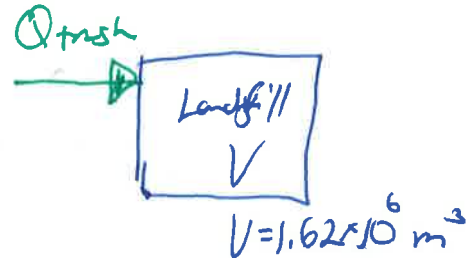
Average depth of landfill = 10 m, so

$$\text{Volume of landfill} = 1.62 \times 10^6 \text{ m}^3$$

Trash is dropped of 5 days a week and compacted to half of its volume, so volumetric flow of trash into landfill,  $Q$  can be expressed as follows:

$$Q = 765 \frac{\text{m}^3}{\text{day}} \times \frac{1 \text{ m}^3}{2 \text{ compaction factor}} \times \frac{5 \text{ days}}{\text{y}} \times \frac{52 \text{ weeks}}{\text{year}} = 99,450 \frac{\text{m}^3}{\text{y}}$$

$$\text{Time to fill landfill} = \frac{\text{Volume of Landfill}}{Q} = \frac{1.62 \times 10^6 \text{ m}^3}{99,450 \frac{\text{m}^3}{\text{day}}} = 16 \text{ years}$$



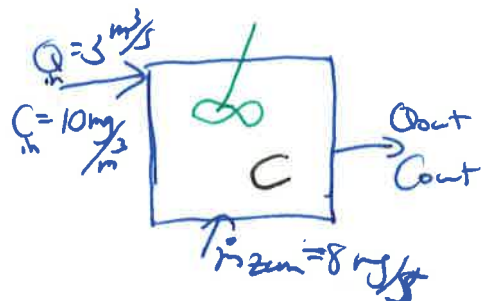
#### 8. Zamboni 13 pt

Given: Steady state (zamboni operating for a long time); well-mixed rink; with CO, a conservative (non-reactive) pollutant

$$Q_{\text{in}} = 3.0 \frac{\text{m}^3}{\text{s}}$$

$$C_{\text{in}} = 10 \frac{\text{mg}}{\text{m}^3}$$

$$\dot{m}_{\text{zamboni}} = 8 \frac{\text{mg}}{\text{s}}$$



(a) Calculate mass flux of CO into the rink:

$$\dot{m}_{\text{in}} = Q_{\text{in}} \times C_{\text{in}} + \dot{m}_{\text{zamboni}} = 3.0 \frac{\text{m}^3}{\text{s}} \times 10 \frac{\text{mg}}{\text{m}^3} + 8 \text{ mg/s} = 38 \frac{\text{mg}}{\text{s}}$$

(b) Calculate the concentration of CO in the rink:

Write the general mass balance equation:

$$\frac{dm}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_{\text{rxn}}$$

But  $\frac{dm}{dt} = 0$ , because system is at steady state.

And  $\dot{m}_{\text{rxn}} = 0$ , because CO is conservative.

$$0 = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} = Q_{\text{in}} \times C_{\text{in}} + \dot{m}_{\text{zamboni}} - Q_{\text{out}} \times C_{\text{out}}$$

But  $C_{\text{out}} = C_{\text{rink}}$ , because system is completely mixed.

And  $Q_{\text{out}} = Q_{\text{in}}$ , because the volumetric flow rate of the zamboni is negligible. Note that you still need to account for the mass flow rate of CO from the zamboni, which is not negligible.

$$0 = Q \times C_{\text{in}} + \dot{m}_{\text{zamboni}} - Q \times C_{\text{rink}}$$

Rearrange:

$$C_{\text{rink}} = \frac{Q \times C_{\text{in}} + \dot{m}_{\text{zamboni}}}{Q} = \frac{3 \frac{\text{m}^3}{\text{s}} \times 10 \frac{\text{mg}}{\text{m}^3} + 8 \frac{\text{mg}}{\text{s}}}{3 \frac{\text{m}^3}{\text{s}}} = 13 \frac{\text{mg CO}}{\text{m}^3}$$