Problem Set 3—Key

CENG 340–Introduction to Environmental Engineering
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Questions

1. Precipitation–Dissolution

$$CaCO_3 \xrightleftharpoons{K_{sp}} [Ca^{2+}] + [CO_3^{2-}]$$

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 10^{-8.3}$$

Since equilibrium occurs at the **end point of a reaction**, we need to calculate the final concenrations of Ca^{2+} and Ca^{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:

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

$$[CaO_3^{2-}] = 50\,\frac{mg}{L} \times \frac{1\,g}{1000\,mg} \times \frac{1\,mole}{60\,g} = 1.25 \times 10^{-3}\,\frac{moles}{L}$$

Table 1: Rice Diagram

Reaction	$\mathbf{Ca^{2+}}$	$\mathbf{CO_3^{2-}}$	$\mathbf{CaCO_3}$
Initial	$8.3 \times 10^{-4}\,\frac{mole}{L}$	$1.25 \times 10^{-3}\,\frac{mole}{L}$	
Change	-x	-x	
Equilibrium	$(8.3 \times 10^{-4} - x)\,\frac{mole}{L}$	$(1.25 \times 10^{-3} - x)\,\frac{mole}{L}$	

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

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = (8.3 \times 10^{-4} - x) \times (1.25 \times 10^{-3} - x) = 10^{-8.3}$$

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. Precipitation–Dissolution of Iron Hydroxide

$$\text{FeOH}_3 \xrightleftharpoons{K_{sp}} [\text{Fe}^{3+}] + [\text{OH}^-]$$

$\text{pK}_{sp} = 38.57$

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

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

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

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

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

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

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

3. Calculate alkalinity in mg/L as $CaCO_3$:

$$[HCO_3^-] = 111\frac{\text{mg}}{\text{L}} \times \frac{1\,\text{mole}}{61\,\text{g}} \times \frac{1\,\text{g}}{1000\,\text{mg}} \times \frac{1\,\text{eq}}{\text{mole}} = 1.8 \times 10^{-3}\,\frac{\text{eq}}{\text{L}}\,\text{of alkalinity}$$

$$[CO_3^{2-}] = 17\frac{\text{mg}}{\text{L}} \times \frac{1\,\text{mole}}{60\,\text{g}} \times \frac{1\,\text{g}}{1000\,\text{mg}} \times \frac{1\,\text{eq}}{\text{mole}} = 5.7 \times 10^{-4}\,\frac{\text{eq}}{\text{L}}\,\text{of alkalinity}$$

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

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. Acid-Base Equilibrium for HOCl in drinking water.
Calculate fraction of HOCl that is in the dissociatead form:

$$[HOCl]_{aq} \xrightleftharpoons{K_a} [H^+]_{aq} + [OCl^-]_{aq}$$

pka = 7.5

$K_a = 10^{-7.5}$

Since it's drinking water, assume pH = 7.

$H^+ = 10^{-7}$

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

Rearrange equation, and substitute values for K_a and H^+:

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

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

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

5. Atrazine

6. Oil Spill nineteen years ago:

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

(a) Try a zero order rate equation:

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

After integration:

$$C = C_0 - kt$$

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

Solve for $k = 20\ t_{-1}$, 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:

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

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

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

Second Order:

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

Rearrange and solve for k:

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

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

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

In conclusion the “worst-case scenario” is second order, in which case, it would take 333 y for the pollutant to degrade. However, first order is more likely.

7. Landfill

8. Zamboni