

Problem Set 3—Key

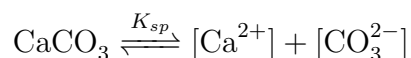
CENG 340—Introduction to Environmental Engineering

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Questions

1. 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 Ca^{2+} and 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	Ca^{2+}	CO_3^{2-}	CaCO_3
Initial	$8.3 \times 10^{-4} \frac{\text{mole}}{\text{L}}$	$1.25 \times 10^{-3} \frac{\text{mole}}{\text{L}}$	
Change	-x	-x	
Equilibrium	$(8.3 \times 10^{-4} - x) \frac{\text{mole}}{\text{L}}$	$(1.25 \times 10^{-3} - x) \frac{\text{mole}}{\text{L}}$	

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

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

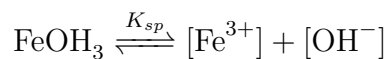
Solve for x.

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

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

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

2. 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. Calculate alkalinity in mg/L as CaCO_3 :

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

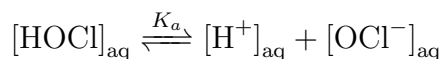
$$[\text{CO}_3^{2-}] = 17 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mole}}{60 \text{ g}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ eq}}{\text{mole}} = 5.7 \times 10^{-4} \frac{\text{eq}}{\text{L}} \text{ of alkalinity}$$

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

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

4. 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. Atrazine

6. 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:

$$C = C_0 - kt$$

$$\text{where } C_0 = 400 \frac{\text{mg}}{\text{g}}$$

$$C = 20 \frac{\text{mg}}{\text{g}}$$

$$t = 19 \text{ year}$$

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:

$$C = \frac{C_0}{1 + C_0 k t}$$

Rearrange and solve for k :

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

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

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

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