

CE4591 Environmental Engineering Chemical Processes, Fall 2008  
Problem Set 6

Due: Friday, 11/21 by 5 p.m.

Solutions will be posted on the Web. Problem sets will be graded for completeness, and one problem (selected at random) will be graded in detail. Each problem set contributes 2.5% towards your final grade. Remember that for problems done with MINEQL, you must print out and attach the header file so that I can see your input.

1. Problem 15.3 (p. 454) in the text. Realize that the  $\text{CaCO}_3$  is added to pure water. Some  $\text{CaCO}_3$  is added to pure water that is open to the atmosphere; not all of the solid dissolves and the equilibrium pH is 8.1. What is the solubility product for  $\text{CaCO}_3$ ?

**SOLUTION:** The solubility product will be for the reaction:



and the solubility product will be defined as:

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

Thus, to find the solubility product, we need to know the activities of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . Because it is an open system, the  $\text{CO}_2$  activity can be calculated from the pH (8.1) and the  $p\text{CO}_2$  in the atmosphere (370  $\mu\text{atm}$ ).

$$K_a = (\text{H}_2\text{CO}_3^*/\text{CO}_2) = 10^{-6.3} \text{ (mole/L-ster)}$$

$$\Rightarrow [\text{H}_2\text{CO}_3^*] = (10^{-6.3} \text{ (mole/L-ster)})(370 \times 10^{-6} \text{ atm}) = 1.2 \times 10^{-9}$$

$$K_{a1} = (\text{HCO}_3^-/\text{H}^+)(\text{H}_2\text{CO}_3^*)$$

$$\Rightarrow [\text{HCO}_3^-] = K_{a1} [\text{H}_2\text{CO}_3^*]/[\text{H}^+] = 6.7 \times 10^{-6} \text{ M}$$

$$K_{a2} = (\text{CO}_3^{2-}/\text{H}^+)(\text{HCO}_3^-)$$

$$\Rightarrow [\text{CO}_3^{2-}] = K_{a2} (\text{HCO}_3^-)/[\text{H}^+] = 3.95 \times 10^{-9} \text{ M}$$

To obtain the  $[\text{Ca}^{2+}]$  activity, it is suggested that we use the charge balance equation:

$$[\text{H}^+] + 2[\text{Ca}^{2+}] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

If activity coefficients are ignored, all quantities (except  $[\text{Ca}^{2+}]$ ) are known, so we can rearrange to solve for this unknown:

$$[\text{Ca}^{2+}] = 1/2 ([\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+]) = 1/2 (10^{-5.9} + 6.7 \times 10^{-6} + 2(3.95 \times 10^{-9}) - 10^{-8.1})$$

$$[\text{Ca}^{2+}] = 4.0 \times 10^{-6} \text{ M}$$

Continuing to ignore activity coefficients, the solubility product would be:

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = (4.0 \times 10^{-6})(3.95 \times 10^{-9}) = 1.58 \times 10^{-14} = 10^{-14.2}$$

This value is close to the solubility product for Dolomite ( $10^{-14.3}$ ). This discrepancy arises in part because we ignored activity coefficients and thereby underestimated the  $[\text{Ca}^{2+}]$  concentration.

2. Problem 15.5 (p. 455) in the text. Use MINEQL. The mineral name for  $\text{Mn}(\text{OH})_2$  is pyrochroite, and for  $\text{MnCO}_3$  is rhodochrosite. Part C will require some thinking. Solubility diagrams can be generated directly in MINEQL or the data can be copied to the clipboard and pasted into Excel for graphing.

15.5A. Draw a solubility diagram for  $[\text{Mn}^{2+}]$  as a function of pH if  $\text{Mn}(\text{OH})_2$  controls the Mn solubility and  $\text{MnCO}_3$  does not exist. Assume a total dissolved carbonate concentration of  $2 \times 10^{-6}$  M.

**SOLUTION:** This problem is easily solved using MINEQL. We must be sure that  $\text{H}_2\text{O}$ ,  $\text{H}^+$ ,  $\text{Mn}^{2+}$ , and  $\text{CO}_3^{2-}$  are checked as components. The header file would contain:

```
MINEQL+ Header file for pyrochroite.mdb
```

# Ce4501 Environmental Engineering Chemical Processes Fall

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## **Table of Contents Ce4501 Environmental Engineering Chemical Processes Fall**

1. Understanding the eBook Ce4501 Environmental Engineering Chemical Processes Fall
  - The Rise of Digital Reading Ce4501 Environmental Engineering Chemical Processes Fall
  - Advantages of eBooks Over Traditional Books
2. Identifying Ce4501 Environmental Engineering Chemical Processes Fall
  - Exploring Different Genres
  - Considering Fiction vs. Non-Fiction
  - Determining Your Reading Goals
3. Choosing the Right eBook Platform
  - Popular eBook Platforms
  - Features to Look for in an Ce4501 Environmental Engineering Chemical Processes Fall
  - User-Friendly Interface
4. Exploring eBook Recommendations from Ce4501 Environmental Engineering Chemical Processes Fall
  - Personalized Recommendations
  - Ce4501 Environmental Engineering Chemical Processes Fall User Reviews and Ratings
  - Ce4501 Environmental Engineering Chemical Processes Fall and Bestseller Lists
5. Accessing Ce4501 Environmental Engineering Chemical Processes Fall Free and Paid eBooks
  - Ce4501 Environmental Engineering Chemical Processes Fall Public Domain eBooks
  - Ce4501 Environmental Engineering Chemical Processes Fall eBook Subscription Services
  - Ce4501 Environmental Engineering Chemical Processes Fall Budget-Friendly Options

6. Navigating Ce4501 Environmental Engineering Chemical Processes Fall eBook Formats
  - ePub, PDF, MOBI, and More
  - Ce4501 Environmental Engineering Chemical Processes Fall Compatibility with Devices
  - Ce4501 Environmental Engineering Chemical Processes Fall Enhanced eBook Features
7. Enhancing Your Reading Experience
  - Adjustable Fonts and Text Sizes of Ce4501 Environmental Engineering Chemical Processes Fall
  - Highlighting and Note-Taking Ce4501 Environmental Engineering Chemical Processes Fall
  - Interactive Elements Ce4501 Environmental Engineering Chemical Processes Fall
8. Staying Engaged with Ce4501 Environmental Engineering Chemical Processes Fall
  - Joining Online Reading Communities
  - Participating in Virtual Book Clubs
  - Following Authors and Publishers Ce4501 Environmental Engineering Chemical Processes Fall
9. Balancing eBooks and Physical Books Ce4501 Environmental Engineering Chemical Processes Fall
  - Benefits of a Digital Library
  - Creating a Diverse Reading Collection Ce4501 Environmental Engineering Chemical Processes Fall
10. Overcoming Reading Challenges
  - Dealing with Digital Eye Strain
  - Minimizing Distractions
  - Managing Screen Time
11. Cultivating a Reading Routine Ce4501 Environmental Engineering Chemical Processes Fall
  - Setting Reading Goals Ce4501 Environmental Engineering Chemical Processes Fall
  - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Ce4501 Environmental Engineering Chemical Processes Fall
  - Fact-Checking eBook Content of Ce4501 Environmental Engineering Chemical Processes Fall
  - Distinguishing Credible Sources
13. Promoting Lifelong Learning
  - Utilizing eBooks for Skill Development
  - Exploring Educational eBooks
14. Embracing eBook Trends
  - Integration of Multimedia Elements

- Interactive and Gamified eBooks

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