

1. Carbonate/CO₂ equilibria, and ramifications.

a) Calculate the solubility of CaCO₃ (s) in H₂O. Assuming no reaction between CO₃⁻² and H₂O takes place ($K_{sp}=4.9 \times 10^{-9}$).

b) Now, consider the reaction between CO₃⁻² and H₂O, add this to the reaction in “a”. Calculate the equilibrium constant for the net reaction, and use it to (re)calculate the solubility of CaCO₃.

c) Explain the increase in solubility (between a & b) in terms of *LeChatlier's principle*.

d) Calculate the pH of a saturated solution of CaCO₃ (using results from b).

e) Suppose the water reservoir in question was such that CaSO₄ minerals were present in the sediments, rather than CaCO₃. What would the pH be in this “solution” if it were saturated w/ CaSO₄ (s)?

$K_{sp}(\text{CaSO}_4) = 2.4 \times 10^{-5}$ and $K_b(\text{SO}_4^{-2}) = 8.3 \times 10^{-13}$.

f) How, ultimately does the predominance of SO₄⁻² over CO₃⁻² rather affect the system's ability to buffer acid input.

2. In class, we discussed how dissolved CO₂ enhanced the solubility of CaCO₃ – and vice versa. Explain both of these effects in terms of *LeChatlier's Principle*, and identify a couple of *positive feedback* loops in this process.

3. Oxidation numbers:

a) Calculate oxidation numbers for both elements in the following: CO₂, CO₃⁻², CH₄, H₂S, SO₄⁻², NH₄⁺, NO₃⁻

b) Which would be referred to as “oxidized” C, S, or N species, and which would be “reduced” C, S, N?

4. a) What is the main oxidant in the *hydrosphere* (the Earth's water reserves)?

b) What are its two main sources?

c) What is the main sink for this oxidant (the primary reducing species)?

d) Why is the concentration of this oxidant such a key parameter in overall water quality assessment?

5. a) The Henry's Law constant (K_H) of water at 25°C is 1.3×10^{-3} M/atm. Use this to calculate the solubility of O₂ in water (units of M and ppm).

b) The solubilities of O₂ at 15°C and 35 °C 10.13 and 7.07 ppm, respectively, use these data to calculate the Henry's Law constants at these temperatures.

Bonus question: Based on the results of “b”, is the process of dissolving O₂ in water *endothermic* or *exothermic*?

c) *Thermal pollution* refers to the (potentially unwelcome) addition of heat to some ecosystem – such as pumping warm water from a power plant into a cold lake. What negative effect would such an activity have?

6. a) Define the quantity pE.

b) Does a high pE value mean the water is oxidizing or reducing? What about a low pE value?

c) In class we noted the pE value for an anaerobic water reservoir, based on the equilibrium between “oxidized carbon” (i.e. CO₂) and “reduced carbon” (CH₄), and found it to be negative. Based on this, what negative effect might result from a large injection of reduced carbon into a stream or river? (This is the case with a manure spill, or even when manure is spread over frozen ground such that it runs off before it sinks into the soil. The additional nutrient load due to the nitrogen (i.e. reduced nitrogen, NH₃) would only amplify the problem.)

7. Describing the chemistry of a thermally stratified lake. Consider the sources and sinks of dissolved oxygen, the pE scale, and answer the questions below.

a) Above the *thermocline* (the top layer of the lake):

- i) Would the conditions be described as *aerobic* or *anaerobic*?
- ii) In terms of sources and/or sinks of dissolved O₂ – why?
- iii) Would the pE value be high or low (perhaps relative to that below the thermocline)?

b) Below the *thermocline* (the bottom layer of the lake):

- i) Would the conditions be described as *aerobic* or *anaerobic*?
- ii) In terms of sources and/or sinks – why?
- iii) Would the pE value be high or low (perhaps relative to that above the thermocline)?

8. Explain how H⁺ input from acid rain can lead to significant concentrations of aqueous Al³⁺ ions (Al(OH)₃ is quite insoluble), and how this leads to fish mortality in acidified waters.

9. Ocean pH has decreased by about 0.1 pH units from a (variable) average of 8.2. How would this change affect CO₃⁻² concentrations, and what are the ecological ramifications.

10. pH/pE Digrams: e.g below...

- a) What is the primary sulfur species present at pH = 8 and pE=0.
- b) What is the primary carbon species present at pE=0 and pH=7.
- c) What is the primary nitrogen species present at pH=7 and pE=0.

