

**PRACTICE PROBLEMS IN CARBONATE CHEMISTRY**

There was interest by many students in being able to improve their problem solving skills in carbonate chemistry. This set gives you some practice opportunities for different solution strategies. Try each before looking at solution set.

1. Here are some “recipes” for water solutions. What is the alkalinity in each of the following systems:
  - a.  $[\text{NaOH}]_T = 10^{-3} \text{ M}$ ,  $[\text{NaHCO}_3]_T = 10^{-2} \text{ M}$ ,  $P_{\text{CO}_2} = 10^{-2.5} \text{ atm}$
  - b.  $[\text{Na}_2\text{CO}_3]_T = 10^{-4} \text{ M}$ ,  $P_{\text{CO}_2} = 10^{-3.0} \text{ atm}$
  - c. A carbonate system with  $\text{pH} = 7.3$  and  $P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$
  - d.  $[\text{H}_2\text{SO}_4]_T = [\text{NaHCO}_3]_T = 10^{-3} \text{ M}$
  
2. Calculate the pH given:
  - a.  $\text{Alk} = C_T = 10^{-3} \text{ M}$
  - b.  $P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$ ,  $\text{Alk} = 10^{-3} \text{ eq/L}$
  - c.  $\text{Alk} = -10^{-2} \text{ eq/L}$  (negative alk = “mineral acidity”)
  
3. The epilimnion of your backyard pond has pH 7.0 and alkalinity  $\sim 10^{-3} \text{ M}$ .
  - d. Assuming the carbonate system dominates the chemistry, calculate the concentration of all carbonate species. Is your pond at equilibrium with the atmosphere? Explain why or why not.
  - e. You just washed the bricks on the patio surrounding the pond with “muriatic acid” (HCl) and some of this washes into the pond. How many eq/L of HCl can you add to the pond epilimnion before changing the pH by more than 0.2 units?
  - f. The buffer capacity of a water can be defined as
$$\beta_H = -\frac{\text{Total Strong Acid Added}}{\Delta\text{pH}}$$
This is a measure of the ability of a system to resist pH changes upon addition of strong acids or bases. What is the buffer capacity of your pond epilimnion?

- g. The hypolimnion of your pond is anoxic. Its composition is derived from that of the epilimnion water by reducing  $2 \times 10^{-3} \text{ M SO}_4$  to  $\text{HS}^-$ . Assume the  $P_{\text{CO}_2}$  is the same in both. What are the alkalinity, the pH, and the concentration of all carbonate species in the hypolimnion?
- h. In the fall, the epilimnion (1 m depth) and hypolimnion (2 m depth) completely mix. Initially there is no exchange of  $\text{CO}_2$  with the atmosphere because of slow exchange kinetics. In this period immediately after mixing, what is the composition (alk, pH, species concentrations) of the resulting water?

**Hints:** This is a classic example of what happens to pH when two waters of different compositions mix, a very common situation in nature.

First off, do *not* try to find the mixed pH by just taking the weighted average of the two previous pHs!! It doesn't work that way. The secret here is to use the fact that Alk is conserved and  $C_T$  is (at least initially) conserved. You need to average those values in the mixture and use those results to calculate pH and speciation.

So, start by adding up the total Alk and total  $C_T$  in both epilimnion and hypolimnion (use the relative depths to get the right proportions) and dividing them into the total volume of pond water (depth). [You actually don't need to know pond area because the relative volumes equal the relative depths].

The new (mixed) Alk will still be about equal to the  $[\text{HCO}_3^-]$ , the  $[\text{CO}_3^{2-}]$  will still be negligible, so you can get the new  $[\text{H}_2\text{CO}_3^*]$  from the difference of  $(C_T - \text{Alk})$ . With that info, you can calculate pH and the rest of the speciation. Be brave, give it a try!!