CH 302 Spring 2008 Worksheet 8 Answer Key

1. NaH_2PO4 (conc. = $C_{NaH2PO4}$) is dissolved in water. Write the mass balance equation for this system.
Answer: $C_{NaH2PO4}$ = $[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

2. Write the charge balance equation for the solution in question 1.
Answer: $[H^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$

3. Write the charge balance equation for a solution containing all of the following ions: H^+, OH^-, Na^+, Ba^{2+}, PO_4^{3-}, Ag^{3+}, SO_4^{2-}, and $COOH^-$.
Answer: $[H^+] + [Na^+] + 2[Ba^{2+}] + 3[Ag^{3+}] = [OH^-] + [COOH^-] + 2[SO_4^{2-}] + 3[PO_4^{3-}]$

4. NaH_2PO_4, $LiHCO_3$, HCl, NaCl, and LiOH are all dissolved in water. How many equations are needed to completely describe this system?
Answer: In solution, we have: H^+, OH^-, Na^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, Li^+, H_2CO_3, HCO_3^-, CO_3^{2-}, and Cl^-. So we need 12 equations.

5. Write a charge balance equation for the system described in question 4.
Answer: $[H^+] + [Na^+] + [Li^+] = [OH^-]\ [Cl^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [HCO_3^-]$
$+ 2[CO_3^{2-}]$

6. Write the mass balance equation for H_2CO_3 (conc. = C_{H2CO3}) in water.
Answer: $C_{H2CO3} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

7. Find the pH of 10^{-8} M HCl like you would have for the last two quizzes. Then find it using the exact expression, $[H^+]^2 - [H^+]C_{HCl} - K_w = 0$. Compare the two answers.
Answer: Like the last two quizzes:

$[H^+] = C_a + 10^{-7} = 1.1 \times 10^{-7}$ pH = 6.96

Exactly:

Solving the quadratic equation yields: $[H^+] = 1.05 \times 10^{-7}$ pH = 6.98

The exact solution is a slightly higher pH because the extra H^+ from the HCl causes a shift in the water equilibrium to the left, resuling in a lower $[H^+]$.

8. Repeat the same thing as in question 7, this time for 10^{-2} M HCl.
Answer: Same work, so I'll just give the answers:

Like the last two quizzes: pH = 2

Exactly: pH = 2

So the water equilibrium really doesn't matter in this case.

9. Assuming an appropriate C_{HCl}, derive the approximate equation for a strong acid, $[H^+] = C_a$, from the expression given in question 6.
Answer: Assuming C_a is large, and since HCl is strong, $[H^+]C_a >> K_w$. So we get:

$[H^+]^2 - [H^+]C_a - K_w \approx [H^+]^2 - [H^+]C_a = 0$

Divide by $[H^+]$ $[H^+] - C_a = 0$ $[H^+] = C_a$

10. In class, you were showen that the exact $[H^+]$ for a weak acid is given by

$$[H^+]^3 + K_a[H^+]^2 - (K_w+K_aC_a)[H^+] - K_aK_w = 0$$

Assuming appropriate values for K_a and C_a, derive the approximate equation for a weak acid, $[H^+] = (K_aC_a)^{1/2}$, from this expression.

Answer: K_w is small and we assume K_a is small "enough," so $K_aK_w \approx 0$.

$$[H^+]^3 + K_a[H^+]^2 - (K_w - K_aC_a)[H^+] = 0$$

$$[H^+]^2 + K_a([H^+] - C_a) - K_w = 0$$

Weak acids barely dissociate, so $[H^+] << C_a$. Furthermore, $[H^+]^2$ and $K_a[H^+]$ are both much larger than K_w. Thus, we get

$$[H^+]^2 - K_aC_a = 0$$

$$[H^+] = (K_aC_a)^{1/2}$$

11. What is the pH of a 0.05 M H_2SO_4 solution if $K_{a2} = 1.1 \times 10^{-2}$? (In class, Dr. Laude did this using a RICE expression and ignored the water equilibrium. Feel free to use his same approach.)

Answer: Setting up the first RICE expression, assuming complete dissociation of the storng acid, at equilibrium you have 0.05 M HSO_4^- and 0.05M H^+. The second equilibrium produces the equation $x^2 + 0.061 \times 10^{-2}x - 5.5 \times 10^{-4} = 0$ which yields the root $x = 0.007974$ which is the amount of H^+ produced in the second dissociation. When added to the 0.05 M H^+ from the first dissociation, the total $H^+ = 0.0579$ M or a pH of 1.2.

12. Rank the concentrations of ions and neutrals at equilibrium in the solution formed in problem 11. Use some common sense reasoning to explain your answer without doing any calculations.

Answer: $H_2O >> H^+ >> HSO_4^- >> SO_4^= > OH^- > H_2SO_4$

H_2O is 55 M so it is largest. We assume H_2SO_4 dissociates completely and is 0 M so it is the smallest concentration. In the RICE expression H^+ and HSO_4^- are produced equally in the first dissociation, but some of the HSO_4^- dissociates to form $SO_4^=$ and H^+ so the total H^+ is slightly higher than the HSO_4^-. The $SO_4^=$ is the result of the second dissociation and so it is less than HSO_4^-. The OH^- will be very small because the solution is strongly acidic.

For Questions 13-20, list the species present in solution and write the system of equations that can be used to solve for their concentrations at equilibrium exactly. You don't have to actually solve the system (but if you're an engineer, go for it).

13. HF (conc. = C_{HF}) in water

Answer: We have H^+, OH^-, and F^-. So we need 3 equations.

$$K_w = [H^+][OH^-]$$

$$K_a = [H^+][F^-]/[HF]$$

$$[H^+] = [OH^-] + [F^-]$$

14. HCl (conc. = C_{HCl}) in water

Answer: We have H^+, OH^-, and Cl^-. So we need 3 equations.

$$K_w = [H^+][OH^-]$$

$[H^+] = [OH^-] + [Cl^-]$

$C_{HCl} = [Cl^-]$

15. HCl (conc. = C_{HCl}) and NH_4Cl (conc. = C_{NH4Cl}) in water

Answer: We have H^+, OH^-, Cl^-, NH_3, and NH_4^+. So we need 4 equations.

$K_w = [H^+][OH^-]$

$K_a = [H^+][NH_3]/[NH_4^+]$

$[H^+] + [NH_4^+] = [OH^-] + [Cl^-]$

$[Cl^-] = C_{HCl} + C_{NH4Cl}$

$C_{NH4Cl} = [NH_4^+] + [NH_3]$

16. $Ba(OH)_2$ (conc. = $C_{Ba(OH)2}$) in water

Answer: We have H^+, OH^-, and Ba^{2+}. So we need 4 equations.

$K_w = [H^+][OH^-]$

$[Ba^{2+}] = C_{Ba(OH)2}$

$[H^+] + 2[Ba^{2+}]= [OH^-]$

17. HCOOH (conc. = C_{HCOOH}) in water

Answer: We have H^+, OH^-, and $COOH^-$. So we need 3 equations.

$K_w = [H^+][OH^-]$

$K_a = [H^+][COOH^-]/[HCOOH]$

$[H^+] = [OH^-] + [COOH^-]$

18. NaOH (conc. = C_{NaOH}) in water

Answer: We have H^+, OH^-, and Na^+. So we need 3 equations.

$K_w = [H^+][OH^-]$

$C_{NaOH} = [Na^+]$

$[H^+] + [Na^+] = [OH^-]$

19. NaOH (conc. = C_{NaOH}) added to a beaker containing Na^+ ions at a concentration of C_{Na}

Answer: We have H^+, OH^-, and Na^+. So we need 3 equations.

$K_w = [H^+][OH^-]$

$C_{NaOH} + C_{Na} = [Na^+]$

$[H^+] + [Na^+] = [OH^-]$