CH 302 Worksheet 10 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 lower pH because the extra H^+ from the HCl causes a shift in the water equilibrium to the left, resuling in a higher $[H^+]$.

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 $[H^+]$ $\qquad [H^+] - C_a = 0 \qquad [H^+] = C_a$

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 <u>exactly</u>. 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.

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

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

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