

## CH 302 Spring 2007 Worksheet 8 Answer Key

1.  $\text{NaH}_2\text{PO}_4$  (conc. =  $C_{\text{NaH}_2\text{PO}_4}$ ) is dissolved in water. Write the mass balance equation for this system.

**Answer:**  $C_{\text{NaH}_2\text{PO}_4} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$

2. Write the charge balance equation for the solution in question 1.

**Answer:**  $[\text{H}^+] = [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}]$

3. Write the charge balance equation for a solution containing all of the following ions:  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Ag}^{3+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{COOH}^-$ .

**Answer:**  $[\text{H}^+] + [\text{Na}^+] + 2[\text{Ba}^{2+}] + 3[\text{Ag}^{3+}] = [\text{OH}^-] + [\text{COOH}^-] + 2[\text{SO}_4^{2-}] + 3[\text{PO}_4^{3-}]$

4.  $\text{NaH}_2\text{PO}_4$ ,  $\text{LiHCO}_3$ ,  $\text{HCl}$ ,  $\text{NaCl}$ , and  $\text{LiOH}$  are all dissolved in water. How many equations are needed to completely describe this system?

**Answer:** In solution, we have:  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Li}^+$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{Cl}^-$ . So we need 12 equations.

5. Write a charge balance equation for the system described in question 4.

**Answer:**  $[\text{H}^+] + [\text{Na}^+] + [\text{Li}^+] = [\text{OH}^-] + [\text{Cl}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$

6. Write the mass balance equation for  $\text{H}_2\text{CO}_3$  (conc. =  $C_{\text{H}_2\text{CO}_3}$ ) in water.

**Answer:**  $C_{\text{H}_2\text{CO}_3} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$

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

**Answer:** Like the last two quizzes:

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

Exactly:

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

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

8. Repeat the same thing as in question 7, this time for  $10^{-2}$  M  $\text{HCl}$ .

**Answer:** Same work, so I'll just give the answers:

Like the last two quizzes:  $\text{pH} = 2$

Exactly:  $\text{pH} = 2$

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

9. Assuming an appropriate  $C_{\text{HCl}}$ , derive the approximate equation for a strong acid,  $[\text{H}^+] = C_a$ , from the expression given in question 6.

**Answer:** Assuming  $C_a$  is large, and since  $\text{HCl}$  is strong,  $[\text{H}^+]C_a \gg K_w$ . So we get:

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

Divide by  $[\text{H}^+]$

$$[\text{H}^+] - C_a = 0$$

$$[\text{H}^+] = C_a$$

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

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

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

**Answer:**  $K_w$  is small and we assume  $K_a$  is small “enough,” so  $K_a K_w \approx 0$ .

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

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

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

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

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

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 strong acid, at equilibrium you have 0.05 M  $HSO_4^-$  and 0.05 M  $H^+$ . 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:**  $H_2O \gg H^+ \gg HSO_4^- \gg SO_4^{2-} > OH^- > H_2SO_4$

$H_2O$  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  $SO_4^{2-}$  and  $H^+$  so the total  $H^+$  is slightly higher than the  $HSO_4^-$ . The  $SO_4^{2-}$  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.

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

$$[\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-]$$

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

15. HCl (conc. =  $C_{\text{HCl}}$ ) and  $\text{NH}_4\text{Cl}$  (conc. =  $C_{\text{NH}_4\text{Cl}}$ ) in water

**Answer:** We have  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_3$ , and  $\text{NH}_4^+$ . So we need 4 equations.

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$K_a = [\text{H}^+][\text{NH}_3]/[\text{NH}_4^+]$$

$$[\text{H}^+] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{Cl}^-]$$

$$[\text{Cl}^-] = C_{\text{HCl}} + C_{\text{NH}_4\text{Cl}}$$

$$C_{\text{NH}_4\text{Cl}} = [\text{NH}_4^+] + [\text{NH}_3]$$

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

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

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{Ba}^{2+}] = C_{\text{Ba}(\text{OH})_2}$$

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

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

**Answer:** We have  $\text{H}^+$ ,  $\text{OH}^-$ , and  $\text{COOH}^-$ . So we need 3 equations.

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$K_a = [\text{H}^+][\text{COOH}^-]/[\text{HCOOH}]$$

$$[\text{H}^+] = [\text{OH}^-] + [\text{COOH}^-]$$

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

**Answer:** We have  $\text{H}^+$ ,  $\text{OH}^-$ , and  $\text{Na}^+$ . So we need 3 equations.

$$K_w = [\text{H}^+][\text{OH}^-]$$

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

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-]$$

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

**Answer:** We have  $\text{H}^+$ ,  $\text{OH}^-$ , and  $\text{Na}^+$ . So we need 3 equations.

$$K_w = [\text{H}^+][\text{OH}^-]$$

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

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-]$$